

# **CO<sub>2</sub> Impurities and LCO<sub>2</sub> Carrier Design: Practical Considerations**



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## **1** INTRODUCTION

The carbon value chain, which includes core elements like carbon capture, utilization, storage and transportation, is an integrated process for carbon emissions management, from source to potential utilization or sequestration.

As companies worldwide increase their carbon capture projects, transporting the captured carbon dioxide  $(CO_2)$  becomes essential. Ships built to transport liquefied carbon dioxide  $(LCO_2)$  as cargo are emerging as a vital link in the carbon value chain. These vessels help ensure  $LCO_2$  is transported safely and efficiently from capture sites to utilization or storage facilities.

This publication explores the challenges of transporting  $LCO_2$  by sea on specialized ships, focusing on the impact of impurities, as assessed in existing literature. It also provides a brief overview of the role and the challenges of  $CO_2$  transportation within the broader carbon capture, utilization and storage (CCUS) value chain. Carbon capture, utilization and storage plays a crucial role in achieving climate goals, and  $CO_2$  transport is a key component for its deployment.

## 2 OVERVIEW OF THE CCUS VALUE CHAIN

Understanding and improving the carbon value chain becomes increasingly important as the globe steps up its efforts to combat climate change. As it scales up, it will become apparent that the maritime industry is at the center of making this value chain a reality, as it accounts for a substantial portion of global trade.

Once extracted,  $CO_2$  can be utilized for a variety of applications. Captured  $CO_2$  can be used for everything from chemical and fuel production to boosting agricultural yields.

While CO<sub>2</sub> transportation has long been a practice in the food industry and oil industry for enhanced oil recovery (EOR), the new carbon capture projects involving various emitters, CO<sub>2</sub> producers and dedicated receivers across large geographical regions introduces new challenges. The most important among these challenges is the varying composition of CO<sub>2</sub> due to impurities, particularly in the marine transportation of LCO<sub>2</sub> at low operating pressures.

#### 2.1 Role of CCUS in Decarbonization

The CCUS value chain begins with capturing  $CO_2$  from emission sources, including power generation or industrial facilities. The captured  $CO_2$  is then transported to its destination either in gaseous or liquid form. While carbon capture is a vital link in the value chain, it still requires more technological development.

The value chain is completed using the captured  $CO_2$  as a feedstock or permanently storing it underground. A proven example is the EOR technique of injecting  $CO_2$  into existing oil fields. Figure 1 illustrates the main elements of the CCUS value chain.



Figure 1: Carbon capture value chain.

The International Energy Agency (IEA) highlighted the importance of CCUS in achieving global climate goals. It is one of the few technologies that can directly reduce CO<sub>2</sub> emissions from heavy industries, such as cement and steel production, which are rarely decarbonized.

The rapid global deployment of CCUS technologies has accelerated in recent years, driven by increasing climate commitments and advancements in capture and storage systems. According to data from the Global CCS Institute, the number of operational and planned CCUS projects worldwide has significantly grown, with over 300 projects now at various stages of development as of the end of 2024. This expansion highlights the importance of addressing technical factors that impact CCUS efficiency, including examining CO<sub>2</sub> impurities. As CO<sub>2</sub> capture scales up across industries, understanding and mitigating the effects of impurities on transport and storage processes have become critical to ensuring the reliability and safety of these systems.

#### 2.1.1 Carbon Capture Technologies

Carbon capture technologies are gaining significant traction due to their retrofit potential to existing emission sources, such as power plants and industrial facilities.

Post-combustion capture is one of the most mature and widely deployed onshore carbon capture technologies. This process involves the separation of  $CO_2$  from flue gas after combustion. Post-combustion capture technologies can be divided into several subcategories based on the method used to capture  $CO_2$ .

Pre-combustion capture involves the conversion of fossil fuels into a mixture of hydrogen and  $CO_2$  before combustion through a process known as reforming. The resulting  $CO_2$  is captured, and the hydrogen can be used as a low-carbon fuel.

Oxy-fuel combustion capture is a process that burns fossil fuels in nearly pure oxygen instead of air, resulting in a flue gas that is primarily  $CO_2$  and water, making the  $CO_2$  easier to capture.

In addition to the above, direct air capture, an emerging technology that captures CO<sub>2</sub> directly from the ambient air rather than from specific emission sources, could also be part of the decarbonization solutions.

#### 2.1.2 Geological Storage

Permanent  $CO_2$  storage projects play a key role in global climate change mitigation efforts, as denoted by the Zero Emission Platform (ZEP) [4]. There are a few permanent geological storage options to consider for  $CO_2$ , such as in saline aquifers or depleted reservoirs. One of the most common and proven solutions is offloading  $CO_2$  to oil and gas wellheads (offshore and onshore) where the  $CO_2$  would be used as a method of EOR while simultaneously being permanently stored.

Injection activities offshore, including existing oil and gas platforms and facilities – both fixed and floating – can be involved in injecting  $CO_2$  for EOR or storage. In the latter case it may not be possible to reuse infrastructure if it was not designed and constructed with  $CO_2$  injection service in mind. Geological sequestration of  $CO_2$  is performed with the substance as a supercritical fluid, i.e., above its critical temperature and pressure on the phase diagram (See Figure 5). Due to differences in fluid pressure, temperature and necessary material properties, as previously mentioned concerning potential corrosion, pitting or cracking, it's impossible.

#### 2.1.3 Utilization

Aside from treating it as a waste for permanent storage,  $CO_2$  is also a key input in many industries. As presented in the ABS publication *Carbon Capture, Utilization and Storage*, the current demand for  $CO_2$  is around 230 million tonnes (Mt) globally per year, and the fertilizer industry alone consumes 125 Mt per year as a raw material in urea manufacturing. Oil and gas producers use around 70 to 80 Mt annually for EOR. Carbon dioxide is also integral for food and beverage production, cooling, water treatment and agriculture, but the demand is relatively small. Additionally,  $CO_2$  is utilized in the chemical industry: indicatively mentioned Sabatier synthesis (methane production), Fischer-Tropsch synthesis (liquid hydrocarbon (HC) production), hydrogenation to methanol and hydrogenation to formic acid.

The processing of the  $CO_2$  stream differs from processing  $CO_2$  for sequestration since  $CO_2$  suitable for EOR or other industrial uses will not likely be fit for food and beverage production, and the purity impacts the carriage requirements.

#### 2.2 Role of CO<sub>2</sub> Transportation in the Carbon Value Chain

Analyzing the role of CO<sub>2</sub> transportation should be concluded in order to build a complete CCUS business model, including understanding challenges, evaluating suitable methods, and considering engineering parameters. The development of new carbon capture projects from various emitters, and the necessity to sequestrate it in dedicated receivers in larger geographical areas make CO<sub>2</sub> transport an essential factor in enabling the deployment of CCUS.

Transport of  $CO_2$  for sequestration requires the implementation of both a coordinated and efficient transportation network. The two main options for large-scale transport are pipelines and ships. Such pipelines are the most obvious solution, particularly where a constant flow from the  $CO_2$  capture sites is required. Where economies of scale do not justify pipelines as the transportation method in a CCUS project, other possibilities include ships, railways and motor carriers [1].

#### 2.2.1 Pipeline Transportation at Supercritical Conditions

Pipeline transport has been practiced for many years on a large scale. There are extensive networks of pipelines used for  $CO_2$  providing injection media for enhanced oil recovery operating for over 50 years in the oil and gas industry. As mentioned by Rahmanian, nearly 360,000 kilometers (km) of pipelines may be required to transport the  $CO_2$  captured from industrial processes by 2050. The U.S. projects to construct between 17,700 and 37,000 km additional  $CO_2$  pipelines before 2050 [2].

For offshore storage, the CCUS industry will build a similar infrastructure to typical ones for oil and gas distribution. Terminal facilities will be needed to transition from land to subsea pipelines or ships. Subsea pipeline and termination manifolds, as well as riser connections to fixed or floating offshore platforms, are also already under study.

The transportation of the CO<sub>2</sub> stream occurs in pipelines above 73.8 bar and a temperature of 31.° C to keep it in a supercritical state. Pipelines are designed and constructed for the required temperature and pressure characteristics and use necessary materials to avoid corrosion, pitting or cracking when considering the content of the CO<sub>2</sub> stream (e.g., accompanying water, nitrogen, hydrocarbons, oxygen, sulfur and sulfides). Risk management should consider inspections, maintenance, leak detection and other means to reduce the likelihood of a release and to minimize its extent in case a release does occur.

#### 2.2.2 Shipping Transportation as Liquid – LCO<sub>2</sub> Carriers

Although pipelines are an established mode of CO<sub>2</sub> transportation, they require a continuous flow of compressed gas, and their costs are highly dependent on distance. Additionally, with the global expansion of CCUS, transporting CO<sub>2</sub> by ships presents a unique business case, particularly for remote emitters over long distances and smaller quantities. Figure 2 illustrates a projection of carbon trading routes based on previous ABS analysis. The importance of transporting CO<sub>2</sub> by ship has been recognized at the European Union (EU) level; in the European Taxonomy for Sustainable Activities and the EU Emissions Trading System (ETS) Directive, as well as at a national level, such as the Dutch SDE++ subsidy scheme and the United Kingdom's CCUS program [3].



Figure 2: Global carbon trade routes projection.

Unlike the supercritical conditions required for transportation through pipelines,  $CO_2$  is currently transported as  $LCO_2$  with ships. At the range of temperatures and pressures used for  $LCO_2$ , its volume is approximately 1/500th of the  $CO_2$ 's volume at standard temperature and pressure.

Figure 3 presents a schematic of the shipping chain from the source to storage. It illustrates the process of capturing  $CO_2$  from a power plant, liquefying and storing it, loading it onto an  $LCO_2$  carrier and delivering it to the final port of destination, where it connects to the endpoint transmission line.

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Figure 3: Carbon dioxide shipping chain [1].

Transfers from ship-to-ship or from ship to floating platform will require detailed analysis of the relative motion parameters to support the design of the transfer system, similar to recent developments for the liquefied natural gas (LNG) ship-to-ship transfer systems.

On a global scale, the total cross-border movement of captured CO<sub>2</sub> within the CCUS ecosystem via shipping could approach ~170 MtPA by 2050, driven by routes in both Asia Pacific and Europe. Globally, the number of vessels required to facilitate this would range from 100 to 200, depending on realized shipping routes globally and the capacity of the vessels for Europe [29].

The current fleet includes seven  $LCO_2$  carriers in service and six on order, with deliveries planned for 2025 to 2026 (See Table 1).

Among the vessels in service, one – the *Excool* – is used for research and development and serves as a demonstration project for the transportation of CO<sub>2</sub> (conducted by Japan's New Energy and Industrial Technology Development Organization – NEDO) and is owned by Sanyu Kisen. Four other vessels are currently serving the food and beverage industry, transporting small capacities (~1,700 tons CO<sub>2</sub>) at operating pressures of 15 to 19 bar(a). The remaining two vessels in service, with a capacity of 7,500 cubic meters (m<sup>3</sup>) at operation pressure of 13 to 18 bar(g), support the Northern Lights project.

Shipyard	Туре	gt	Built	Status	Company
Hyundai Mipo	LCO <sub>2</sub> /LPG Carrier	21,034	2025	On Order	Capital Gas
Hyundai Mipo	LCO <sub>2</sub> /LPG Carrier	21,034	2026	On Order	Capital Gas
Hyundai Mipo	LCO <sub>2</sub> /LPG Carrier	21,034	2026	On Order	Capital Gas
Hyundai Mipo	LCO <sub>2</sub> /LPG Carrier	21,034	2026	On Order	Capital Gas
DSOC	LCO <sub>2</sub> Carrier	8,035	2025	On Order	Northern Lights
DSOC	LCO <sub>2</sub> Carrier	8,035	2026	On Order	Schulte Group
DSOC	LCO <sub>2</sub> Carrier	8,035	2024	In Service	Northern Lights
DSOC	LCO <sub>2</sub> Carrier	8,035	2024	In Service	Northern Lights
Royal Bodewes SY	LCO <sub>2</sub> Carrier	2,506	2005	In Service	Nippon Gases Europe
Royal Bodewes SY	LCO <sub>2</sub> Carrier	2,506	2005	In Service	Nippon Gases Europe
Royal Bodewes SY	LCO <sub>2</sub> Carrier	2,474	2004	In Service	Nippon Gases Europe
Frisian Shyd.	LCO <sub>2</sub> Carrier	1,825	1999	In Service	Nippon Gases Europe
MHI Shimonoseki	LCO <sub>2</sub> Carrier	996	2023	In Service	Sanyu Kisen

*Table 1: LCO<sub>2</sub> carrier in service and orderbook/ABS analytics.* 

Techno-economical assessments have shown that LCO<sub>2</sub> will predominantly be transported at cryogenic conditions [5].

Currently, no ship transports  $CO_2$  in the 6 to 8 bar(g) pressure range. However, significant progress is being made in joint industry projects, such as the one between Ecolog, Hanwha Ocean, Babcock LGE and ABS, which recently issued an approval in principle (AIP) for a low-pressure, 40,000 m<sup>3</sup> LCO<sub>2</sub> carrier. Unlike onshore  $CO_2$ handling systems and transportation by pipelines, the lack of comprehensive engineering data presents certain challenges during the feasibility study stage for low-pressure transportation. These challenges include the cargo handling at low pressure near the  $CO_2$  triple point and ensuring appropriate material selection.

## 3 BASIS OF DESIGN FOR LCO<sub>2</sub> CARRIERS: PARAMETERS AND CONDITIONS FOR DESIGN

The design of the cargo tanks must comply with the International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk, (IGC Code). The IGC Code has been the basis for the design of cargo tanks for liquefied petroleum gas (LPG) carriers since the 1960s.

While most designs take into consideration pure  $CO_2$ , the development of  $LCO_2$  carriers requires a comprehensive understanding of the behavior of  $CO_2$  as cargo. Impurities that may exist in the mixture of different carbon capture methods and processes can have a significant impact on:

- Health and safety matters with toxic substances
- Thermophysical properties of CO<sub>2</sub> mixture (phase diagram, density)
- · Corrosivity and material selection (corrosion through reactions, free water)
- Reliquefication plant design (incondensable)

#### 3.1 Health and Safety Matters

The primary hazard of  $CO_2$  is that it can be designated as an asphyxiant, while at high concentrations it can also be classified as toxic. Table 2, taken from a publication by the Society of International Gas Tanker and Terminal Operators (SIGTTO) [28], summarizes the exposure limits from various standards.

Source	Threshold limit value (TLV) (ppm)	Short-term exposure limit (STEL) (ppm)
HSE (U.K.) [6]	5,000 (8 hours)	15,000 (15 minutes)
OSHA (U.S.) [7]	5,000 (8 hours)	-
NIOSH (U.S.) [8]	5,000 (10 hours)	30,000 (15 minutes)
ACGIH (U.S.) [9]	5,000 (8 hours)	30,000 (15 minutes)
Directives 91/322/EEC [10] and 2000/39/EC (EU) [11]	5,000 (8 hours)	-
Ordinance on Health Standards in the Office (MHLW Japan) [12]	5,000 (8 hours), 40 hours/week	-
GBZ2.1-2019 (China) [13]	5,000 (8 hours)	9,000 (15 minutes)

Table 2: CO<sub>2</sub> toxicity levels.

#### 3.2 Thermophysical Properties (Phase Diagram, Density)

Carbon dioxide is a non-flammable gas at atmospheric pressure and ambient temperature. It can be liquefied at various pressures between the triple point (5.18 bar(a), -56.6° C for pure  $CO_2$ ) and critical point (73.8 bar(a), 31.1° C). Figure 4 illustrated the phase diagram of  $CO_2$ .



Figure 4: Phase Diagram of CO<sub>2</sub> with pressure areas of transportation [3].

Consideration of the physical properties of  $CO_2$  is crucial to the design parameters of the tanks, specifically the vapor-liquid phase behavior of  $CO_2$ . Tables 3 and 4 summarize the Norwegian Ministry of Petroleum's assessment of vessel transportation of  $CO_2$  under three different conditions. Although the report concludes that these solutions are technologically feasible, a number of different considerations must be carefully evaluated. Low-pressure conditions, although associated with higher propensity for dry-ice formation due to the proximity to the triple point, enhance cargo efficiency due to its high-density state.

Condition	Low-pressure	Medium-pressure	High-pressure
	(0.7-0.8 MPa, 223 K)	(1.5 MPa, 248 K)	(4.5 MPa, 283 K)
Advantages	<ul> <li>High density</li> <li>Established know-how</li></ul>	<ul> <li>Commercially mature</li></ul>	<ul> <li>Low conditioning costs</li> <li>Most appropriate</li></ul>
	on LPG experience <li>Scalable tank size and</li>	concept in the food and	condition for direct-
	ships	brewery industries	injection from ship
Challenges	<ul> <li>Proximity to solid phase</li> <li>High conditioning costs</li> <li>Complex insulation</li> </ul>	<ul> <li>Relatively high volume of steel in the tank</li> <li>Technically challenging tank structure</li> </ul>	<ul> <li>Complex design of tanks</li> <li>Low TRL</li> <li>Low density</li> <li>Risk for cold boiling liquid expanding vapor explosion (BLEVE)</li> </ul>

Table 3: General assessment of alternative transport conditions for CO<sub>2</sub> shipping [1].

	Low-pressure	Medium-pressure	High-pressure
Temperature (° C)	-55 to -40	-30 to -20	0 to 15
Pressure Bar(g)	5 to 10	15 to 20	35 to 50
Density (kg/m³)	1,170 to 1,120	1,080 to 1,030	930 to 820
Tonnes cargo weight per m³	1.2 to 1.1	1.1 to 1.0	0.9 to 0.8

## Table 4: Pressure and temperature of the three conditions considered for CO<sub>2</sub> transportation [14].

For reference,  $CO_2$  at ambient conditions has a density of approximately 1.8 kg/m<sup>3</sup>, while at liquid phase (close to -50° C and 7 bar(a)) it reaches approximately 1,100 kg/m<sup>3</sup>. A higher density means more  $CO_2$  mass can be transported under a fixed volume. For  $LCO_2$ , the density increases when the pressure is reduced due to the lower equilibrium temperature.

### 3.3 Corrosivity and Material Selection (Corrosion Through Reactions, Free Water)

Type C tanks are considered the most suitable for LCO<sub>2</sub> transportation and are traditionally cylindrical or bi-lobe shapes arranged in vertical or horizontal configurations. Plate thickness is correlated to design pressure and governs the maximum diameter and tank capacity.

The material selection must account for the low-temperature operating conditions. According to the  $CO_2$  phase diagram, a pressure of 6 bar(g) corresponds to a temperature of -50° C, which is close to the limit for carbon-manganese steel. If the pressure is higher, higher steel plate thickness will be required, increasing the tank weight, complexity of tank construction, and weldability. These factors limit the tank capacity and increase the number of cargo tanks required to achieve the desired carrying capacity.

For the case of LCO<sub>2</sub> carriers, material selection should always comply with the IGC Code's Chapter 6 requirements for steel plates up to 40 mm thickness. Above 40 mm and up to 50 mm, IACS UR W1 applies. As per IGC Code 6.6.2.2, post-weld heat treatment (PWHT) is required. An exemption to post-weld stress relief heat treatment based on an alternative approach (e.g., engineering critical assessment) must be approved by the classification society or adhere to recognized standards.

Table 5 shows the materials currently used for the  $LCO_2$  carriers under construction in the shipyards. While 5 percent and 9 percent nickel steels can be suitable for  $LCO_2$  applications, they are typically more expensive. New carbon-manganese steel materials of higher strength, such as LT51 and F550, are being developed by steel mills and are subject to approval from classification societies.

	LT36	P690
Specific Min. Yield Strength (MPa)	355	690
Specific Min. Tensile Strength (MPa)	490	770 to 940
Application	Low-pressure	Medium-pressure

Table 5: LCO<sub>2</sub> cargo tank materials.

Among others, the challenge with the above is the composition of the  $CO_2$  stream. The quantitative impact of the impurities in the  $CO_2$  mixture needs to be investigated through proper research for shipboard transportation.

## 4 CO<sub>2</sub> QUALITY SPECIFICATIONS AND BEHAVIOR AS A CARGO

Commercializing  $CO_2$  for industrial applications such as welding, food and beverage production, chemical manufacturing, medical application and laboratory use requires strict requirements concerning purity grades. The presence of impurities, even in trace amounts, can cause interference or contamination. For instance, in the U.S., the Food and Drug Administration (FDA) mandates that beverage-grade  $CO_2$  purity cannot contain more than 0.09 percent hydrocarbons. In the EU, the European Commission (EC) regulates food-grade  $CO_2$  with stated minimum purity criteria for food-grade gases such as  $CO_2$ , nitrogen and oxygen. Each must adhere to a number code and must be of high purity.

Using  $CO_2$  as a waste product requires a different approach. The fundamental question for the carbon value chain is: What is the composition of the  $CO_2$  cargo?

Currently, there are no commercial drivers to establish a standard for permissible impurity levels in CO<sub>2</sub> for carbon capture and storage (CCS). Existing agreements, such as those for EOR, are business-specific, with requirements for the CO<sub>2</sub> compositions defined in contracts between suppliers, transporters, and storage operators [15]. However, one significant challenge in the future CCUS business model is the varying impurity compositions from different sources that may have practical, health, safety and/or environmental impacts on CO<sub>2</sub> transport and storage systems.

The commonly accepted minimum  $CO_2$  stream purity is greater than 95 percent mole (mol), aligning with the guidance given in ISO/TR 27921:2020 [13 to 16].

### 4.1 CO<sub>2</sub> Stream Composition and Cross Cutting Issues for CCUS and LCO<sub>2</sub> Carriers

Currently, there are no established standards for CO<sub>2</sub> as shipping cargo, but only project-specific recommendations. The experience of the marine industry and knowledge of the impact of impurities comes from onshore systems and EOR processes. This publication examines the type of impurities and their potential impact on the vessel design by addressing any cross cutting issues, emphasizing the need for simulation and experiments.

The ISO/TR 27921:2020 technical report provides information about the gas composition in carbon capture, transportation and geological storage, but due to limited data and understanding, it does not define a fixed maximum concentration of a single impurity when other impurities are or may be present [16].

The  $CO_2$  stream composition affects the design and operation of the entire carbon value chain, including the capture process, final purification, transportation and sequestration. However, it is difficult to identify thresholds for individual impurities for two main reasons:

- Site-specific risk studies are usually carried out by operators, assessing project-specific data and environmental factors.
- The impacts due to the interaction between multiple impurities and their surroundings can differ from those of a single impurity in the CO<sub>2</sub> stream.

As a result, impurity concentration thresholds are case-specific and subject to optimization for the entire CCUS process with respect to safety, environmental protection, cost and energy demand.

#### 4.2 Common Impurities in the CO<sub>2</sub> Stream

The CO<sub>2</sub> captured from various sources contains a variety of trace gases depending on the chemistry of the source's feedstock, the carbon capture technology, the solvents or absorbents utilized, and the downstream clean-up technology deployed. As per the ISO document, recognized impurities in a CO<sub>2</sub> stream typically include the following:

- Oxygen (O<sub>2</sub>)
- Water (H<sub>2</sub>O)
- Nitrogen (N<sub>2</sub>)
- Hydrogen (H₂)
- Sulfur oxides (SO<sub>x</sub>)
- Nitrogen oxides (NO<sub>x</sub>)
- Hydrogen sulfide (H₂S)
- Hydrogen cyanide (HCN)
- Carbonyl sulfide (COS)
- Ammonia (NH₃)
- Amines
- Aldehydes
- Particulate matter (PM)

Two primary factors determine how impurities affect CCUS systems:

- Physical effects: Impact on phase behavior and transport conditions
- Chemical effects: Corrosivity, toxicity and interactions with materials

#### 4.2.1 Sources of CO<sub>2</sub> Impurities

The source of impurities depends on the sourcing process, the capturing technology and the additional separation or purification process. Table 6 illustrates an indicative CO<sub>2</sub> composition based on the following capturing technologies:

- Pre-combustion
- Post-combustion
- Oxy-fuel

The composition of  $CO_2$  impurities is similar in pre- and post-combustion capture methods, whereas the oxy-fuel capture method produces a significantly different composition of certain impurities.

Impact	Component	Post-combustion	Pre-combustion	Oxy-fuel
	CO <sub>2</sub>	> 98 vol% purity	> 98 vol% purity	> 85 vol% purity
Corrosion	H <sub>2</sub> O	Before Compression: High moisture up to 5% by mass. After Compression: < 2200 ppmv. Needs further drying.	Depends on the solvent. < 600 ppmv. No need further drying.	High moisture up to 20% by weight depending on the moisture content in coal.
Corrosion and Compression	O <sub>2</sub>	Low, < 2 to 3%	Low, < 2 to 3%	High, < 5%
Corrosion and Health and Safety	H₂S	Low levels	Low, up to 100 ppm (depending on separation process)	Low levels
Compression	N <sub>2</sub>	Low, < 2 to 3%	Low, < 2 to 3%	High, < 6%
Compression	H <sub>2</sub>	Low, < 2 to 3%	Low, < 2 to 3%	
Compression	Ar	Low, < 2 to 3%	Low, < 2 to 3%	High, < 5%
Compression	CH₄	Low, < 2 to 3%	Low, < 2 to 3%	
Health and Safety	HCN			
Compression	O <sub>2</sub>	Low, < 2 to 3%	Low, < 2 to 3%	High, < 5 %
Corrosion	СО	Low concentration levels (20 ppm)	Low concentration levels (400 ppm)	Low concentration levels (50 ppm)
Health and Safety	SO <sub>2</sub>	Low STEL levels (Requires SO <sub>2</sub> levels of < 10 ppmv to reduce amine losses)	Low concentration levels	High SO <sub>2</sub> depending on sulfur content of the fuel (up to 2,000 ppmv)
Health and Safety	NO <sub>x</sub>	Low concentration levels (< 20 ppm)	Virtually zero concentration levels	Higher NO <sub>x</sub> content when compared to combustion on air (< 100 ppm)
Health and Safety	Hg	Below detectable levels	Below detectable levels	Needs separation
Health and Safety	Amine			
Health and Safety	Glycol			
Health and Safety	NH <sub>3</sub>	50 ppm		
Health and Safety	CH₃OH		200 ppm	

Table 6: Composition from different technologies [17].

The typical sources of  $CO_2$  are coal and gas refineries, fired power plants, the steel and cement industries, and integrated gasification combined cycle (IGCC) systems. While the composition of impurities in  $CO_2$  streams is generally similar across sources, there are some notable variations depending on the specific source. However, aside from these variations, the composition of impurities is largely independent of the  $CO_2$  source.

The World Resources Institute's CCS Guide offers detailed information about the composition of impurities based on different  $CO_2$  sources. Additional insights can be found in projects such as Sintef's IMPACT and the Northern Lights initiative in Norway, which consolidate data on impurities by emission activity.

Table 7 provides an overview of the expected CO<sub>2</sub> stream compositions for six CO<sub>2</sub> sources and their associated capture technologies responsible for the most extreme impurity levels. Concentrations are provided on a volume basis, with values expressed in parts per million (ppm) unless otherwise indicated as a percentage.

CO₂ source Capture technology	Coal-fired power plant Amine-based absorption	Coal-fired power plant Ammonia- based absorption	Coal-fired power plant Selexol- based absorption	Coal-fired power plant Oxy-fuel combustion	Natural gas processing Amine-based absorption	Synthesis processing Rectisol- based absorption
CO2	98.8%	99.8%	98.2%	95.3%	95.0%	96.7%
N <sub>2</sub>	2,000	2,000	6,000	2.5%	5,000	30
O <sub>2</sub>	200	200	1	1.6%		5
Ar	100	100	500	6,000		
NOx	50	50		100		
SO <sub>x</sub>	10	10		100		
со	10	10	400	50		1,000
H₂S			100		200	9,000
H <sub>2</sub>			1.0%			500
CH₄			1,000		4.0%	7,000
C <sub>2</sub> +					5,000	1.5%
NH₃	1	100				
Amine	1					

Table 7: Overview of expected typical CO<sub>2</sub> stream composition [18].

### 4.2.2 Effects of CO<sub>2</sub> Impurities

Per the design basis of a CCUS system, common impurities are grouped based on three aspects:

- Thermophysical effects on phase boundaries (N $_{2},$  O $_{2},$  Ar, CH $_{4},$  H $_{2})$
- Corrosivity (O<sub>2</sub>, H<sub>2</sub>O, SO<sub>x</sub>, NO<sub>x</sub> H<sub>2</sub>S)
- Health and safety considerations: These are determined by short-term exposure limits (STEL) and long-term exposure limits (LTEL) as per local regulations (include NO<sub>2</sub>, CO, H<sub>2</sub>S, SO<sub>2</sub>, HCN, COS, NH<sub>3</sub>, among others)

Impurities are typically classified into two main types – condensable and non-condensable. Non-condensable impurities are further divided into the following three categories:

- Major impurities: Present at concentrations above 0.5 percent
- Minor impurities: Typically, at ppm levels but less than 0.5 percent
- Micro-impurities: PM with varying composition percentages

Not all impurities impact the system the same way, with some having a more significant influence than others (Refer to Table 8). For instance, non-condensable impurities can alter the thermodynamic and physical properties of the  $CO_2$  stream, such as increasing the saturation pressure and lowering the critical temperature [2, 16, 19, 20].

The impurity composition directly affects several parameters:

- Available volume and mass of containment: High impurity levels can significantly reduce volumetric capacity. For example, a 10 percent hydrogen concentration can reduce capacity by 27 percent.
- Physical properties and transport conditions: Impurities influence compression, liquefaction and power demands.
- Material durability: The composition can impact corrosion, fracture, and failure of metallic and nonmetallic components.
- Hydrate formation: Certain impurities increase the likelihood of hydrates forming in the system.

Component	Limit	Reason	Reference
	300 ppm	To prevent corrosion damages in presence of CO $_2$ , H $_2$ S, SO $_2$ and NO $_x$	Murugan et al., 2020 [5]
Water	< 60% water saturation level in gas stream	Below solubility limit of water in CO <sub>2</sub> .	WRI CCS Guideline, 2008 [6]
	30 lb/MMcf (-600 ppm wt)	Corrosion risk	IEAGHG, 2016 [7]
N <sub>2</sub> , O <sub>2</sub> , Ar	< 4 vol%	Can increase compression required power and decrease storage capacity	De Visser et al., 2008 [8]
O <sub>2</sub>	< 10 ppm	<ul> <li>In CO<sub>2</sub>-EOR application due to growth of bacteria and combustion of hydrocarbons</li> <li>Significant impact on corrosion rate</li> </ul>	Murugan et al., 2020 [5]
H <sub>2</sub>	< 4 vol%	Can increase compression required power and decrease storage capacity	De Visser et al., 2008 [8]
со	< 1,000 ppm 900 to 5,000 ppm	<ul> <li>For CO<sub>2</sub>-EOR applications</li> <li>Health and safety considerations</li> </ul>	Murugan et al., 2020 [5]
H <sub>2</sub> S	200 ppmv	<ul><li>Immediately dangerous to life or health</li><li>Corrosion Risk</li></ul>	NETL, 2012 [9]
SO <sub>2</sub>	100 ppmv	<ul><li>Immediately dangerous to life or health</li><li>Corrosion Risk</li></ul>	NETL, 2012 [9]
NO <sub>x</sub> (NO, NO <sub>2</sub> )	100 ppmv	IDLH level	Sim et al., 2013 [4]
Mercury	Gas processing: <0.01 µg/m³ CO₂-EOR: 0.3 gal/MMcf	Toxicity and corrosion impact on some metals	De Visser et al., 2008 [8]
Particulates	0 to 1 ppmv	<ul> <li>To prevent damage or equipment fouling</li> <li>Can block geological storage pores</li> </ul>	NETL 2012 [9]
Glycol	0.3 gal/MMcf	Process fluid	Murugan et al., 2020 [5]
NH <sub>3</sub>	25 ppm	Toxicity and potential particulate formation with nitric/sulfuric acids	Murugan et al., 2020 [5]

Table 8: Summary of Impurity Specifications in CO<sub>2</sub>-rich Streams and their Impacts in the CCUS Chain [21].

Because of the nature of the impurities, there are effects such as corrosion due to the relation between  $CO_2$  composition and injection and storage and the effects of impurities on the external safety of pipelines and hubs for geological storage.

Thus, a lot of projects are setting requirements for specifications. Some recommended specifications, modeled data and real-life composition data obtained from various projects are available in the literature. The maximum acceptable concentration of some common impurities as per three different projects and the maximum value available in the literature are provided in Table 9. The upper limits may be chosen for safer design and operational flexibility but may be less cost-efficient.

Effects	Constituent		CarbonNet proposed specs	NPL report	Dynamis	Max in lit
	CO <sub>2</sub>	min	97.5% V	95% V	95.5% V	90% V
Corrosion	H <sub>2</sub> O	max	100 ppmv	30 ppmv	500 ppmv	50 ppmm
Compression	N <sub>2</sub>	max	0.8% V	4% V	4% V	4% V
Compression	H <sub>2</sub>	max	0.8% V			4% V
Compression	Ar	max	0.2% V			4% V
Corrosion	O <sub>2</sub>	max	200	50 ppmv	4% V	
Compression	CH <sub>4</sub>	max	500	0.7% V	4% V	4% V
	Other HC	max	2% V			
	Total HC			5% V		
Health and Safety	HCN	max	0.002% V			
Health and Safety	со	max	5,000 ppmv	1,000 ppmv	2,000 ppmv	5,000 ppmv
Corrosion	H <sub>2</sub> S	max	200 ppmv	10,000 ppmm	200 ppmv	1.3% V
Health and Safety	SO <sub>2</sub>	max	2,000 ppmv		100 ppmv	50,000 ppmv
	S	max		35 ppmm		
Health and Safety	NO <sub>x</sub>	max	2,500 ppmv		100 ppmv	2,500 ppmv
Health and Safety	Hg					Stel 0.003 ppmv
Health and Safety	Amine					Stel 6 ppmv
Damage sealing materials	Glycol					174 ppbv
Health and Safety	HF					3 ppmv
Health and Safety	НСІ					5 ppmv
Health and Safety	$C_2H_4O$					50 ppmv
Health and Safety	NH <sub>3</sub>					50 ppmv
Explosive	C <sub>3</sub> H <sub>8</sub>					1% V
Explosive	C <sub>2</sub> H <sub>6</sub>					1% V
	Particulate					1% V

*Table 9: CO<sub>2</sub> composition for different projects.* 

A generic impurity level, based on end-use requirements, as indicated in the ENCAP project (Enhanced Capture of  $CO_2 - EU$  Funded) is provided in Table 10.

Component	Concentration	Limitation
H <sub>2</sub> O	500 ppm	Technical: Below solubility limit of $H_2O$ in $CO_2$ . No significant cross effect of $H_2O$ and $H_2S$ , cross effect of $H_2O$ and $CH_4$ is significant but within limits for water solubility.
H <sub>2</sub> S	200 ppm	Health and safety considerations
со	2,000 ppm	Health and safety considerations
O <sub>2</sub>	Aquifer < 4 volume %, EOR 100 to 1,000 ppm	Technical: Range for EOR, because lack of practical experiments on effects of $O_2$ underground.
CH₄	Aquifer < 4 volume %, EOR < 2 volume %	As proposed in ENCAP project
N <sub>2</sub>	< 4 volume % (all non-condensable gases)	As proposed in ENCAP project
Ar	< 4 volume % (all non-condensable gases)	As proposed in ENCAP project
H <sub>2</sub>	< 4 volume % (all non-condensable gases)	Further reduction of $H_2$ is recommended because of its energy content
SO <sub>x</sub>	100 ppm	Health and safety considerations
NO <sub>x</sub>	100 ppm	Health and safety considerations
CO <sub>2</sub>	> 95.5%	Balanced with other compounds in $\text{CO}_2$

Table 10: Recommended CO<sub>2</sub> Quality for CCS taken from the DYNAMIS project [22].

### 4.3 CO<sub>2</sub> Compositions Requirements for Project Sequestration and Impurities Thresholds

Specifications for  $CO_2$  transportation can vary depending on whether they are designed to meet end-user needs or transport requirements. Additionally, the requirements for transporting  $CO_2$  by ship differ from those for transportation through pipeline. While pipeline transportation of  $CO_2$  is already well-established, shipping transportation is still in its early stages. This is due to a lack of sufficient academic and bibliographic references related to the design and handling of  $CO_2$  cargo, particularly when impurities are present.

### 4.3.1 CO<sub>2</sub> Compositions Requirements for Piping

Before  $CO_2$  is transported through pipelines, it is typically dehydrated to ensure water levels remain below 50 µmol mol-1. Maintaining this threshold is critical to prevent pipeline corrosion and ensure safe operation. According to an article by the World Resources Institute,  $CO_2$  pipelines can be categorized into three main types based on the different purity levels of  $CO_2$  that can be present [15] (Refer to Table 11).

Parameter	Type I	Type II	Type III				
$CO_2 - \%$ by volume	> 95	> 95	> 96				
H <sub>2</sub> S	< 10	< 20	< 10,000				
Sulfur — ppmbw	< 35	< 30	-				
Total hydrocarbons – % by volume	< 5	< 5	-				
$CH_4 - \%$ by volume	-	-	< 0.7				
$C_2$ + hydrocarbons — % by volume	-	-	< 23,000				
CO — % by volume	-	-	< 1,000				
$N_2 - \%$ by volume/weight	< 4	< 4	< 300				
0 <sub>2</sub> — ppm by weight/volume	< 10	< 10	< 50				
$H_2O - #/mmcf^*$ or ppm by volume**	< 25	< 30	< 20				
$C_2$ = carbon: CH <sub>4</sub> = methane: CO = carbon monoxide: CO <sub>2</sub> = carbon dioxide: H <sub>2</sub> O = water: H <sub>2</sub> S hydrogen							

 $C_2$  = carbon;  $CH_4$  = methane; CO = carbon monoxide;  $CO_2$  = carbon dioxide;  $H_2O$  = water;  $H_2S$  hydrogen sulfide; mmcf = millions of cubic feet;  $N_2$  = nitrogen, ppm = parts per million;  $O_2$  = oxygen; ppmbw = ppm by weight

Table 11: Acceptable purity levels of CO<sub>2</sub> for the different types of pipelines used for CO<sub>2</sub> transportation.

Indicatively, a prescribed impurity limit, as indicated in the CO<sub>2</sub> Europipe project, is provided in Table 12.

Impurity	Limit	Impurity	Limit
CO <sub>2</sub>	> 95% by volume	NO <sub>2</sub>	75 ppm
H <sub>2</sub> O	No free water	СО	2,000 ppm
Ar	Together < 5% by volume	H <sub>2</sub> S	200 ppm
CH <sub>4</sub>		HCN	70 ppm
H <sub>2</sub>		SO <sub>2</sub>	75 ppm
N <sub>2</sub>		COS	235 ppm
O <sub>2</sub>		NH <sub>3</sub>	550 ppm

Table 12: CO<sub>2</sub> Europipe Consortium [23].

#### 4.3.2 CO<sub>2</sub> Compositions Requirements for Shipping

The emerging nature of CO<sub>2</sub> shipping and the absence of standardized guidelines for CO<sub>2</sub> cargo containing impurities present significant challenges. Impurities in the CO<sub>2</sub> stream can affect the system's thermodynamic properties, making the prediction of design parameters under cryogenic conditions difficult.

To address these uncertainties, insights from existing literature and the experience from pipeline transportation can be useful guidance for the development of design parameters and risk assessments necessary to obtain qualifications for concept designs.

Based on ZEP studies, there are two standards for the transportation of CO<sub>2</sub> by ships (Refer to Table 13).

Component	Northern Lights <sup>(1)</sup> Concentration (ppm mol)	EU <sup>(2)</sup> Recommendations
Carbon dioxide (CO <sub>2</sub> )	Not defined	> 99.7% by volume
Acetaldehyde	<u>≤</u> 20	Not defined
Amine	<u>≤</u> 10	Not defined
Ammonia (NH₃)	<u>≤</u> 10	Not defined
Argon (Ar)	Not defined	< 0.3% by volume
Cadmium (Cd)/Titanium (Ti)	≤ 0.03 (sum)	Not defined
Carbon monoxide (CO)	<u>≤</u> 100	< 2,000 ppm
Hydrogen (H <sub>2</sub> )	≤ 50	<0.3% by volume
Hydrogen sulfide (H <sub>2</sub> S)	<u>≤</u> 9	< 200 ppm
Formaldehyde	≤ 20	Not defined
Mercury (Hg)	≤ 0.03	Not defined
Methane	Not defined	$\leq$ 0.3% by volume
Nitric oxide/nitrogen dioxide (NO <sub>x</sub> )	<u>≤</u> 10	Not defined
Oxygen (O <sub>2</sub> )	<u>≤</u> 10	Not specified as literature inconsistent
Sulfur oxides (SO <sub>x</sub> )	<u>≤</u> 10	Not defined
Water (H <sub>2</sub> O)	<u>≤</u> 30	≤ 50 ppm

#### Table 13: Two published CO<sub>2</sub> compositions for shipping [14].

Northern Lights published updated LCO<sub>2</sub> quality specifications in February 2024, with stricter specifications on methane, nitrogen, nitrogen oxides, mercury and argon (Refer to Table 14).

Component	Unit	Limit for CO₂ Cargo within Reference Conditions¹	
Carbon dioxide (CO <sub>2</sub> )	mol-%	Balance (Minimum 99.81%)	
Water (H <sub>2</sub> O)	ppm-mol	<u>≤</u> 30	
Oxygen (O <sub>2</sub> )	ppm-mol	<u>≤</u> 10	
Sulfur oxides (SO <sub>x</sub> )	ppm-mol	<u>≤</u> 10	
Nitrogen oxides (NO <sub>x</sub> )	ppm-mol	≤ 1.5	
Hydrogen sulfide ( $H_2S$ )	ppm-mol	<u>≤</u> 9	
Amine	ppm-mol	<u>≤</u> 10	
Ammonia (NH <sub>3</sub> )	ppm-mol	<u>≤</u> 10	
Formaldehyde (CH <sub>2</sub> O)	ppm-mol	<u>≤</u> 20	
Acetaldehyde (CH <sub>2</sub> CHO)	ppm-mol	<u>≤</u> 20	
Mercury (Hg)	ppm-mol	≤ 0.0003	
Carbon monoxide (CO)	ppm-mol	≤100	
Hydrogen (H <sub>2</sub> )	ppm-mol	<u>≤</u> 50	
Cadmium (Cd), Thallium (TI)	ppm-mol	Sum ≤ 0.03	
Methane ( $CH_4$ )	ppm-mol	≤100	
Nitrogen (N <sub>2</sub> )	ppm-mol	<u>≤</u> 50	
Argon (Ar)	ppm-mol	≤100	
Methanol (CH₃OH)	ppm-mol	<u>≤</u> 30	
Ethanol (C <sub>2</sub> H <sub>5</sub> OH)	ppm-mol	<u>≤</u> 1	
Total volatile organic compounds (VOC) <sup>2</sup>	ppm-mol	≤ 10	
Mono-ethylene glycol (MEG)	ppm-mol	<u>≤</u> 0.005	
Tri-ethylene glycol (TEG)	ppm-mol	Not allowed	
BTEX <sup>2</sup>	ppm-mol	<u>≤</u> 0.5	
Ethylene ( $C_2H_4$ )	ppm-mol	<u>≤</u> 0.5	
Hydrogen cyanide (HCN)	ppm-mol	<u>≤</u> 100	
Aliphatic hydrocarbons $(C_2+)^4$	ppm-mol	≤ 1,100	
Ethane ( $C_2H_6$ )	ppm-mol	<u>≤</u> 75	
Solids, particles, dust	ppm-mol	<u>≤</u> 1	

#### *Table: 14: LCO<sub>2</sub> Quality Specifications [24].*

The presence of non-condensable gases in CO<sub>2</sub> streams significantly impacts energy consumption during compression and liquefaction in the case of low-pressure and low-temperature transportation by ship. As the concentration of inert constituents increases, the energy required for these processes rises proportionally. Different impurities affect energy consumption differently. For example [25]:

- A 1 percent concentration of O<sub>2</sub> increases compression work by approximately 2.5 percent.
- A 1 percent concentration of  $N_2$  results in a 3.5 percent increase.
- A 1 percent concentration of  $H_2$  leads to a 4.5 percent increase.
- A 5 percent concentration of  $H_2$  leads to a 25 percent increase.

Table 15 indicates the CO<sub>2</sub> quality recommendations for ship transport.

Component	Concentration	Limitation	Reason
Water (H <sub>2</sub> O)	50 ppm	Design and operational considerations	Freeze-out in heat exchangers
Hydrogen sulfide ( $H_2S$ )	200 ppm	Health and safety considerations	Short-term exposure limit
Carbon monoxide (CO)	2,000 ppm	Health and safety considerations	Short-term exposure limit
Methane (CH₄)	< 0.3% v/v (all non- condensable gases)	Design and operational considerations	Dry ice formation, costs for liquefaction
Nitrogen (N <sub>2</sub> )	< 0.3% v/v (all non- condensable gases)	Design and operational considerations	Dry ice formation, costs for liquefaction
Oxygen (O₂)	Unknown	Literature not consistent	Challenges in the reservoir
Argon (Ar)	< 0.3% v/v (all non- condensable gases)	Design and operational considerations	Dry ice formation, costs for liquefaction
Hydrogen (H <sub>2</sub> )	< 0.3% v/v (all non- condensable gases)	Design and operational considerations	Dry ice formation, costs for liquefaction
Carbon dioxide (CO <sub>2</sub> )	> 99.7% v/v	Balanced with other compounds	Dry ice formation

Table 15: CO<sub>2</sub> quality recommendations for ship transport [25].

### 4.4 Thermophysical Properties of the CO<sub>2</sub> Stream and Cargo Handling

The development of LCO<sub>2</sub> carriers requires a solid understanding of the behavior of CO<sub>2</sub> as cargo. Carbon dioxide is a non-flammable gas at atmospheric pressure and ambient temperature. As previously mentioned, CO<sub>2</sub> can be liquefied at various pressures between the triple point (5.18 bar(a), -56.6° C for pure CO<sub>2</sub>) and critical point (73.8 bar(a), 31.1° C) (Refer to Figure 5). To maximize cargo density, the preferable cryogenic conditions are at low temperature and pressure. However, the composition of the CO<sub>2</sub> stream may affect the thermodynamic properties of the CO<sub>2</sub> stream and impact materials and cargo handling. Table 16 provides an overview of the pysucak and thermodynamic properties and their relevance to CO<sub>2</sub> shipping.



Figure 5: CO<sub>2</sub> phase diagram [26]. © 1999 ChemicaLogic Corporation, Drawn with CO<sub>2</sub> Tab V1.0

Property	Relevance	Remarks	Impurities
Density	Vessel dimensioning, compressor and pump design, carrier stability	Highest near the triple point	N <sub>2</sub> , Ar, H <sub>2</sub> S
Solubility of water	Risk of corrosion and hydrate formation	Limited experimental data covering shipping conditions	CH <sub>4</sub> , N <sub>2</sub> , NO <sub>2</sub> , SO <sub>2</sub> , O <sub>2</sub>
Viscosity	Estimation of pressure drop in the system, Design of process equipment	Liquid viscosity data is limited to CO <sub>2</sub> - H <sub>2</sub> O systems	H₂O
Phase Equilibria	Water solubility, Phase boundaries, Liquid loading/ unloading, Temperature-pressure characteristics	Minimal presence of impurities can alter phase equilibria significantly	H <sub>2</sub> , SO <sub>2</sub> , N <sub>2</sub>

Table 16: Physical and thermodynamic properties and their relevance to CO<sub>2</sub> shipping [1].

#### 4.4.1 Phase Equilibria of CO<sub>2</sub> Mixtures

A comprehensive understanding of pressure, temperature and composition mechanisms is essential to developing appropriate conditioning, transport and storage procedures, as CO<sub>2</sub> will always need to be processed in liquid forms throughout the shipping transport chain. However, there is a lack of vapor-liquid equilibrium (VLE) data relevant to shipping conditions for binary systems such as CO<sub>2</sub>-COS, CO<sub>2</sub>-NO, CO<sub>2</sub>- amines, CO<sub>2</sub>-SO<sub>2</sub> and even more for tertiary systems. This challenge is getting more complicated based on the variable compositions of CO<sub>2</sub> from different emitters and the absence of a common standard CO<sub>2</sub> composition.

Depending on the impurities, the phase boundaries widen and the pressure requirement for single-phase containment changes. For pipeline transportation, impurities increase the critical temperature and pressure and influence the operating region. The two-phase region is not economical or the preferred region of operation.

The presence of non-condensable gases affects the phase behavior of  $CO_2$ . The following non-condensable gases might be present in  $CO_2$ :  $H_2$ , argon (Ar),  $N_2$ ,  $O_2$  and methane ( $CH_4$ ). These non-condensable gases have an extremely low tendency to interact with other materials but will dilute  $CO_2$  making phase change more complex than the normal coexistence of pure  $CO_2$  and  $LCO_2$  at constant pressure and temperature. Their presence also increases the pressure requirements for the condensation of  $CO_2$ .

For pipeline transportation, these non-condensable impurities affect the transport and injection capacity by increasing the critical pressure, consequently causing supercritical transport conditions with higher pressures and higher costs.

For shipping transportation, predicting and managing the behavior of  $LCO_2$  under these conditions is even more critical. Table 17 below shows VLE data on shipping conditions for binary and ternary systems of different impurities.

System	Sources	Points	Temperature (K)	Pressure (MPa)	CO₂ concentrations (mol%)
CO <sub>2</sub> - N <sub>2</sub>	34	> 700	208 to 303	0.6 to 21.4	0.15 to 0.99
CO <sub>2</sub> - O <sub>2</sub>	8	> 292	218 to 298	0.9 to 14.7	0.15 to 0.99
CO <sub>2</sub> - Ar	4	~ 200	233 to 299	1.5 to 14	0.25 to 0.99
CO <sub>2</sub> - H <sub>2</sub> S	8	> 270	248 to 365	1 to 8.9	0.01 to 0.97
CO <sub>2</sub> - CO	3	106	223 to 293	0.8 to 14.2	0.2 to 0.99
CO <sub>2</sub> - H <sub>2</sub>	8	> 400	218 to 303	0.9 to 172	0.07 to 0.99
CO <sub>2</sub> - N <sub>2</sub> - O <sub>2</sub>	3	80	218 to 273	5.1 to 13	0 to 0.93
CO <sub>2</sub> - CO - H <sub>2</sub>	1	36	233 to 283	2 to 20	0.17 to 0.98
CO <sub>2</sub> - CH <sub>4</sub> - N <sub>2</sub>	2	> 100	220 to 293	6 to 10	0.27 to 0.99
CO <sub>2</sub> - CH <sub>4</sub> - H <sub>2</sub> S	1	16	222 to 239	2.1 to 4.8	0.024 to 0.78
CO <sub>2</sub> - CH <sub>4</sub> - H <sub>2</sub> O	5	> 132	245 to 423	0.1 to 100	0.001 to 0.83

Table 17: VLE data for CCUS-relevant systems at shipping conditions [1].



Figure 6 illustrates the effect of impurities on pressure-temperature phase equilibria.

Figure 6: Calculated phase boundaries for mixtures of CO<sub>2</sub> [1].

Different impurities have varying effects on the  $CO_2$  phase envelope. Vapor pressure can increase by as high as 30 percent due to incondensable impurities such as  $H_2$ ,  $O_2$  and  $N_2$ , even at concentrations below 0.5 mol percent. In contrast,  $SO_2$  affects the phase envelope differently. A mixture of 98 mol percent  $CO_2$  and 2 mol percent  $H_2$  exhibits bubble-point pressures of 6.12 MPa and 6.24 MPa at 253 K and 263 K, respectively, higher than the bubble-point pressure of pure  $CO_2$ . The effect of impurities on bubble-point pressures at cryogenic temperatures is summarized in Table 18.

Mixture	Vapor pressure	Mixture	Vapor pressure
100% CO <sub>2</sub>	0.67 MPa	$CO_2$ mixture – 0.05 mol% $O_2$	0.69 MPa
$CO_2$ mixture – 0.05 mol% $N_2$	0.7 MPa	$CO_2$ mixture – 0.05 mol% H <sub>2</sub>	1.03 MPa
$CO_2$ mixture – 0.1 mol% N <sub>2</sub>	0.73 MPa	CO₂ mixture — 0.05 mol% CO	0.7 MPa
$CO_2$ mixture – 0.05 mol% $N_2$	0.97 MPa	CO₂ mixture — 0.05 mol% Ar	0.68 MPa

Table 18: Effect of impurities on equilibrium pressure of CO<sub>2</sub> at 223 K [1].

### 4.4.2 Solubility in CO2 and Challenges

When water dissolves in  $CO_2$ , it forms carbonic acid, which is a highly corrosive substance. The water content of supercritical  $CO_2$  is temperature-dependent. While pure  $CO_2$  with dissolved water below the saturation limit does not corrode carbon steel in operating conditions, it may form hydrates, which can cause blockages in the system. Hydrate formation becomes more problematic at higher operating pressures. A drop in pressure can cause water to separate from the  $CO_2$ , leading to the formation of carbonic acid and creating a corrosive environment. This makes temperature and pressure fluctuations a critical consideration for the design and operation of cargo containment systems.





Figure 7: Solubility of water in Liquid CO<sub>2</sub> [17].



Figure 8: Solubility of water in CO<sub>2</sub> [27]. © SINTEF Energy Research

When  $LCO_2$  carries more water than gaseous  $CO_2$ , the solubility of water in  $CO_2$  abruptly changes during the phase transition of  $CO_2$ . The presence of impurities affects the phase behavior of  $CO_2$  and makes it more corrosive. The solubility of water in  $CO_2$  decreases in the presence of impurities such as  $NO_2$  and  $SO_2$  and, to some extent, in the presence of  $CH_4$ ,  $N_2$  or  $O_2$ . In contrast, the presence of a small amount of  $H_2S$  increases water solubility, and a low water level allows higher concentrations of  $H_2S$  without inducing corrosive effects.

The presence of free water aggravates the formation of solid crystalline hydrate and increases corrosion due to the reaction of water with acidic gases such as  $SO_x$  and  $NO_x$ .

Hydrates are typically formed by low-soluble gases such as  $CO_2$ ,  $CH_4$  and  $H_2S$  above the freezing point of water, and at high pressure. Hydrates can form even without the presence of free water.

To mitigate any risks, the desired water limit in  $CO_2$  should vary from 40 ppm (conservative) to 500 ppm or higher to avoid free water formation. Under normal operating conditions, water's solubility is 1,500 ppm; therefore, dense phase  $CO_2$  containing 500 ppm of water does not pose a high risk of free water formation.

Impurities such as  $H_2S$  and  $SO_x$ , when present at high concentrations, may release elemental sulfur that may deposit or block passages if the temperature exceeds 673 K at compressor discharge. In addition,  $H_2S$  may also cause brittleness. Reactive impurities like  $H_2S$ ,  $O_2$ ,  $SO_x$ ,  $NO_x$ , etc., are corrosive to metallic components and can damage non-metallic seals.

#### 4.4.3 Density of CO<sub>2</sub> and Challenges

The density of  $CO_2$  varies significantly across its phases and is higher near the triple-point. For reference,  $CO_2$  at ambient conditions has a density of approximately 1.8 kg/m<sup>3</sup>, while in the liquid phase (close to -50° C and 7 bar(a)), it reaches approximately 1,100 kg/m<sup>3</sup> and increases when reducing the pressure due to the lower equilibrium temperature (Refer to Figures 9 and 10).



Figure 9: Liquid and saturation liquid densities of CO<sub>2</sub> [1].



Figure 10: Liquid and saturated liquid densities of CO<sub>2</sub> [1].

Density is sensitive to impurities and moderately sensitive to pressure. The molar volume of most impurities is higher than that of  $CO_2$ , reducing the density of the mixture. Non-condensable impurities increase the pressure requirement. The density of saturated  $LCO_2$  is inversely related to the pressure.

Lower-density  $LCO_2$  reduces a ship's volumetric efficiency, and a higher pressure limits tank size and increases the wall thickness.

## **5 CONCLUSION AND KEY TAKEAWAYS**

The increasing demand for  $CO_2$  transportation highlights the critical role of  $LCO_2$  carriers in supporting the global carbon value chain. While pipelines remain a well-established option, shipping offers unique advantages, especially for remote and geographically dispersed emitters. This publication highlights several critical considerations for the design and operation of  $LCO_2$  carriers based on the current understanding of this topic and ABS' work with major shipyards to grant AIPs for  $LCO_2$  carrier designs of various sizes.

- 1. Design and Operational Considerations:
  - a. The design trend is to transport  $CO_2$  at lower pressures closer to the triple point using larger tanks and an increased total capacity.
  - b. Operational pressures for LCO<sub>2</sub> carriers are typically maintained within the 6 to 10 bar(g) range and away from the triple point to ensure safety and efficiency while avoiding dry ice formation.
  - c. Type C tanks, with their robust designs, are the preferred option, but material selection must account for the low-temperature and high-pressure operating conditions.
- 2. Impact of CO<sub>2</sub> Composition:
  - a. Carbon dioxide composition plays an important role in designing these vessels and associated systems. Most designs consider reasonably pure  $CO_2$ .
  - b. The presence of impurities significantly influences thermophysical properties, corrosion potential and cargo handling systems. Variations in CO<sub>2</sub> sources and capture technologies, the solvents or absorbents, and the downstream clean-up technology require flexibility in design specifications.
  - c. Non-condensable gases, such as  $H_2$  and  $N_2$ , increase pressure and energy requirements, while reactive impurities like  $SO_x$  and  $H_2S$  demand careful material selection to mitigate corrosion and operational risks.
- 4. Research Gaps
  - a. A lack of comprehensive VLE data for shipping conditions complicates the prediction of CO<sub>2</sub> phase behavior, particularly with mixtures containing impurities.
  - b. Further research is needed to investigate the quantitative impact of impurities in the  $CO_2$  mixture on shipboard transportation. Without proven data, one safe approach during the design stages is to use appropriate simulation tools and equations of state to predict phase changes for a safe cargo operation and choose suitable materials.

In conclusion, while the transportation of  $LCO_2$  presents unique challenges, it also offers a great opportunity to enable the large-scale deployment of CCUS technologies. Addressing the technical, operational and safety challenges highlighted in this publication will be critical to achieving global climate goals.

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