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CO₂ quality in the shipbased CO₂ capture

context

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1. Document History

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1.1. Revision History

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1.2. Authorisation

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AUTHORISATION	Name	Signature	Date
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2. Executive summary

The EverLoNG project covers multiple aspects of the marinization of CO_2 capture – from technoeconomic to environmental and regulatory aspects. In this deliverable, the quality of captured CO_2 is discussed, in view of expected impurities and the most recent CO_2 specifications from transport and storage CCS projects.

Onboard Carbon Capture (OCC) was demonstrated in EverLoNG onboard 2 vessels. In both campaigns, the impurities content in the exhaust gases and from the OCC pilot were monitored. The most relevant observation made in the context of CO_2 quality is the relatively high NOx content in the exhaust gas of marine engines. At the Technology Centre Mongstad (TCM), a large CO_2 capture pilot plant in Norway, the NOx content in the raw CO_2 is measured at 0.5 ppmv, which is close to the Northern Lights and Aramis specifications (1.5 ppmv¹). However, the reported NO₂ content in the flue gases of TCM is below 2.5 ppmv, whereas in the EverLoNG campaigns values in the 50-250 ppmv range were measured (data publicly shared in EverLoNG webinars²). This indicates that the NOx content in OCC-produced CO_2 will potentially be higher than specifications.

There are different approaches to tackle this challenge. The first would be to (further) remove NOx from the exhaust gases, for instance by applying selective catalytic reduction (SCR) and/or removing NO₂ in the quench column by applying a sulphite-thiosulphate solution (this could also be integrated in a SOx scrubber). The proposed solutions would add to the treating costs onboard, but have the benefit of protecting the amine-based solvent from NO₂-induced oxidative degradation. Alternatively, and if the presence of relatively high NO₂ content in the liquid CO₂ wouldn't affect the onboard storage tanks, the on-shore CO₂ receiving terminals could be equipped with NOx separation technologies.

Future research should focus on: a) measuring the NOx content in the raw and liquid CO_2 in OCC pilots; b) verifying whether the risks of a potentially high NOx content is acceptable for the on-board storage tanks; c) evaluating and comparing different NOx removal technologies, both from technical and economic aspects. In the EverLoNG campaigns as well as in related literature, it was identified that the NO₂ leads to increased rate of oxidative degradation of solvents. This implies increased rate of formation of degradation products. Therefore, monitoring the presence of other impurities, in particular NH₃ and aldehydes in the raw and liquified CO_2 should also be a focus point in future research.

¹ Websites of Northern Lights (<u>NorthernLights-GS-co2-spec2024.pdf</u>) and Aramis (<u>ARM-Template Memo</u>) projects

² Events | EverLoNG, please refer to webinars #1 and #2 for NOx content data and discussions



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3. Introduction

In the EverLoNG project, the feasibility of capturing CO_2 from the exhaust gas emissions of ships is investigated. The technology proposed for CO_2 capture, amine scrubbing, has reached high technology readiness level (TRL9), and is currently being implemented in different industries, such as cement, power and waste-to-energy. While many aspects of the technology are well documented in literature, the quality of the captured CO_2 remains an under-explored topic.

In CO₂ capture with amines, the exhaust gas is contacted with an aqueous solution of amine (in EverLoNG, the 1st generation solvent 30wt% monoethanolamine in water was used), and CO₂ is transferred from the gas to the liquid phase. In this process, also other gases are absorbed in the liquid, albeit to a much lower extent. This includes O₂, N₂, NO, NO₂ and SO₂. Some of these gases are reactive towards amines (O₂, NO₂, SO₂) and will be at least partially reacted, forming amine degradation products and heat stable salts, while other gases are inert (N₂, NO). The molecules that remain dissolved (as opposed to reacted to other products) in the amine solution when it reaches the regeneration side of the process are likely to be stripped along with CO₂, constituting impurities in the raw captured CO₂.

The onboard carbon capture (OCC) concept proposed in EverLoNG includes a CO_2 liquefaction plant onboard, so that the CO_2 can be stored in tanks as a liquid at ca. 20 bar, -20°C. The steps towards liquefaction include compression, cooling and drying, and it is also common for liquefaction plants to be equipped with additional purification steps. This may include an active carbon bed for adsorbing impurities, a catalytic oxidation step for consuming oxygen (e.g., by reacting it with hydrogen, forming water), and a distillation column for removing non-condensables (O_2 , N_2).

The design of the liquefaction plant is generally guided by the CO_2 quality specification, which can be food-grade, or dictated by a CO_2 transport and storage project, such as Northern Lights, Porthos or Aramis. For OCC, we propose that the liquefaction plant is designed only with process constraints in mind. This means that the impurities are separated only to the extent required by the process (e.g., water dew-point to avoid dry ice formation), but without taking any particular specification in mind. We assume that ships equipped with OCC will deliver CO_2 to multiple ports, which will be connected to different transport and storage or utilization projects, and these end-users will have imposed different CO_2 quality specifications. The port-side infrastructure would include a CO_2 purification and re-conditioning unit, so that the pressure, temperature and composition of the CO_2 is adequate to the specific CCUS chain it connects to. This ensures seamless integration between OCC and existing and proposed CCUS projects.

It was the intention of the EverLoNG project to produce data on the composition of the liquefied CO_2 in its 2 on-board demonstration campaigns. However, during the first campaign, the liquefaction unit faced technical challenges and could not be operated. During the second campaign, approximately 1550 kg of CO_2 was successfully liquified and stored on-board in a tank. Unfortunately, potentially due to a mistakenly open valve, all the CO_2 was vented before a sample could be retrieved. Therefore, the project did not achieve its initial target of providing data on CO_2 quality.

Instead, this report offers a discussion on CO_2 quality in the OCC context, which we believe will be useful in informing future scale-up projects.



4. CO₂ quality specifications

While there is no universal CO_2 quality standard, it is common for transport and storage projects to set their own CO_2 quality specifications. These are typically informed by lab experiments made with CO_2 mixed with impurities, in which the phase behaviour of the mixture is observed, as well as its corrosivity. A recent overview of published CO_2 specifications is given in the Industry Guidelines for Setting the CO_2 Specification in CCUS Chains (Wood, 2024).

There is a wide range of variations amongst the projects, as illustrated in Table 1. When considering only the most recent specifications (2020 onwards), specifications for maximum O_2 content range from 10 to 40 ppmv; SOx from 1 to 50 ppmv; and NOx from 1 to 50 ppmv.

		Dynamis	NETL	Longannet	Goldeneye/	CarbonNet	NETL	Porthos	Fluxys	TES	PACE-	Aramis:	Aramis:	AMPP	Northern
			Design		Peterhead	Project	Design		Gas	OGE	CCS Ltd	Pipeline	Ship	Tentative	Lights
	Year	2007	2013	2014	2014 (2016)	2016	2019	2021	2022	2022	2022	2023	2023	2023	2024
	Ref	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[13]	[14]	[15]
	Туре	Generic	Generic	Project Specific	Project Specific	Project Specific	Generic	Project Specific	Project Specific	Project Specific	Generic	Project Specific	Project Specific	Generic	Project Specific
	H ₂ O	500	500	50	50	100	500	70	40	30	50	70	30	100	30
	H ₂ S	200	100	0.5	0.5	100	100	5	5	10		5	5	10	9
_	со	2000	35	10	10	900-5000	35	750	750	100	2000	750	1200	1000	100
[lom-mqd]	O 2	<40000	10	1	1 (5)	20000- 50000	10	40	40	30	10	40	10	20	10
	SOx	100	100	10	10	250-2500	100		10 ^g	1	50		10	10	10
Component	Sulphur comp							20 ^a		30 ^c	5 ^f	20 ^b		20/60 ^d	
lino li	NOx	100	100	10	10	200-2000	100	5	5	1	50	2.5	1.5	2.5/10 ^e	1.5
0	MeOH							620	620		500	620	40		30
	NH₃		50	5			50	3	3	10	1500	3	10		10
	Amine			2				1	1	1		1	10		10

Table 1. CO₂ specifications of various transport and storage projects. Source: Wood, 2024

Notes:

Total sulphur-contained compounds (COS, dimethyl sulphide, H₂S, SO_x, mercaptan) of which H₂S \leq 5 ppm

 $b \qquad H_2S+COS+SO_X+dimethyl \ sulphide$

 $\begin{array}{ll} c & \mbox{Total sulphur} \\ d & \mbox{H}_2S+SO_X+COS, \mbox{ concentration may be increased to 60 ppm-mol if NO}_2 \mbox{ is not present} \end{array}$

e 2.5 ppm is suggested for lower operating temperatures (seabed)

 $f H_2S + COS$

g SO₃ < 0.1 ppm-mol

While Table 1 presents an overview of specifications for different components, it is not exhaustive. For illustration, the complete current specification for the Aramis project is presented in Table 2. We highlight the presence of NH_3 , aldehydes, carboxylic acids and amides within the volatile organic compounds (VOCs). These are oxidative degradation products of amines and are expected to be formed regardless of the amine-based solvent chosen. Oxidative degradation and the formation of some of these components have been followed during the EverLoNG onboard carbon capture demonstrations (see confidential deliverables D1.5.1 and D1.5.2, and public webinars #1 and #3).

Online monitoring of the composition of the CO₂ product is a challenge. Aramis is working with sensor providers to establish methodologies. Nevertheless, recent discussions with Aramis partners, point at the direction of leaving monitoring as a responsibility of the CO₂ supplier, as the project's receiving terminal currently does not include any CO₂ purification steps.



Table 2. CO₂ specifications for the Aramis project. Source: <u>Aramis CCS | CO₂ specifications for Aramis transport</u> <u>infrastructure</u>

Class	Component	Constraint	Unit	Ships	Pipeline infrastructure
	CO ₂	larger than	mol%	balance	95
	H ₂ O	less than	ppmmol	30	70 ⁽¹⁾
inerts	N ₂	less than	mol%	-	2.4
inerts	O ₂	less than	ppmmol	10	40
inerts	H ₂	less than	ppmmol	500	7500
inerts	Ar	less than	mol%	-	0.4
inerts	CH ₄	less than	mol%	-	1
inerts	CO	less than	ppmmol	1200	750
inerts	O ₂ +N ₂ +H ₂ +Ar+CH ₄ +CO	sum less than	ppmmol	2000	40000
	NO _x	sum less than	ppmmol	1.5	2.5 ⁽⁴⁾
sulphur	SOx	sum less than	ppmmol	10	-
sulphur	H ₂ S	less than	ppmmol	5	5
sulphur	CarbonylSulphide	less than	ppmmol	-	_(1)
sulphur	DimethylSulphide	less than	ppmmol	-	_(1)
sulphur	$H_2S + COS + SO_x + DMS$	sum less than	ppmmol	-	20
VOCs	Amine	less than	ppmmol	10	1
VOCs	Formaldehyde	less than	ppmmol	20	-
VOCs	Acetaldehyde	less than	ppmmol	20	_(1)
VOCs	Aldehydes	sum less than	ppmmol	-	10
VOCs	carbolylic acids & amides	sum less than	ppmmol	-	1
VOCs	phosphorus-containing compounds	sum less than	ppmmol	-	1
VOCs	NH ₃	less than	ppmmol	10	3
VOCs	Ethylene (C ₂ H ₄)	sum less than	ppmmol	-	_(1)
VOCs	H-Cyanide (HCN)	less than	ppmmol	-	2
VOCs	Total volatile organic compounds (excl. MeOH, EtOH, aldehydes)	sum less than	ppmmol	10	10
VOCs	Methanol	less than	ppmmol	40	620
VOCs	Ethanol	less than	ppmmol	20	20
Heavies	glycols (TEG)	sum less than		-	Follow dew-point specification
Heavies	C ₂₊ (aliphatic hydrocarbons)	sum less than	ppmmol	-	1200
Heavies	Aromatic Hydrocarbons	sum less than	ppmmol	-	0.1
Metals	Hg	less than	ppbmol	30	-
Metals	Cadmium + Thalium	sum less than	ppbmol	30	-
Dew-point	Dew point (any liquid phase)	sum less than	°C (@ 20 bar)	-	-10 ⁽²⁾
Solids	Full removal cut-off diameter	Less than	micron	1 ⁽³⁾	1 ⁽³⁾



It is unlikely that every OCC ship will be fully equipped with sensors to monitor the quality of the produced CO_2 to ensure meeting the desired specifications. Particularly in cases in which the ships will be delivering CO_2 to various projects (with potentially different specifications). This reinforces the need for CO_2 receiving terminals in the OCC-compliant ports which are equipped with CO_2 purification steps and sensors to monitor the CO_2 quality delivered to downstream CO_2 transport and storage projects.

To our knowledge, apart from the food and beverage sector specifications, there are no CO₂ specifications developed particularly for utilization projects. Many of the CO₂ conversion technologies are (electro)catalytic, and impurities even in the ppb level could potentially affect the downstream processes. One can speculate that CO₂ utilization specifications will be even more stringent when it comes to e.g., sulphur-containing impurities (known to poison catalysts).

Another important consideration is regarding how specifications may vary in time. For instance, the Northern Lights specifications shown in Table 1 are a revised and more stringent version than their previous list. With gained operational experience, it is possible that specifications will evolve and could become either more relaxed or more stringent.

5. Raw CO₂ quality data

Information of impurities present in the raw CO_2 stream, produced out of MEA-based capture plants is only scarcely available in literature. Table 3 shows a compilation of raw CO_2 quality data measured in 2 different campaigns at the Test Center Mongstad (TCM), using MEA as the capture solvent. By raw CO_2 , we mean the CO_2 produced at the stripper top. Many of the products monitored in the 2015 campaign where below the detection limit. Most of the impurities are within the limits of the Aramis specifications, but the results indicate that O_2 and aldehydes would potentially require control.

Component	unit	2015	21-6- 2017	11-7- 2017	13-7- 2017	7-11- 2017	9-11- 2017	17-11- 2017
Acetaldehyde	ppmv	8.51	2.9	6.9	7.1	6.3	6.5	7.7
Formaldehyde	ppmv	0.11	int	int	int	int	int	int
MEA	ppmv	0.030	nd	nd	nd	nd	nd	nd
Diethylamine	ppmv	0.0010	nd	nd	nd	nd	nd	nd
Acetone	ppmv	<0.4	nd	0.2	0.4	0.5	0.4	0.5
O ₂ +Ar	ppmv		49	cont	cont	28	36	17
N2	ppmv		420	cont	cont	220	370	310
СО	ppmv		nd	nd	nd	nd	nd	nd
NOx	ppmv		nd	nd	0.5	0.5	0.5	0.5
тнс	ppmv		4.8	12	10	11	22	9.3

Table 3. Compilation of raw CO₂ quality data from TCM campaigns. Sources: Johnsen et al., 2018 and Flø et al., 2017



NH ₃	ppmv		1	nd	nd	0.5	nd	0.5
Formamide	mg/Sm ³	<0.03						
Acetamide	mg/Sm ³	<0.03						
Dipropylamine	mg/Sm ³	<0.001						
Dimethylamine	mg/Sm ³	<0.00065						
Methylamine	mg/Sm ³	<0.0006						
Ethylamine	mg/Sm ³	<0.0006						
Propylamine	mg/Sm ³	<0.0006						
Ethylmethylamine	mg/Sm ³	<0.0006						
DEA	mg/Sm ³	<0.0003						
TEA	mg/Sm ³	<0.0003						
ΤΟΝΟ	mg/Sm ³	<0.001						
NDMA	mg/Sm ³	<0.0003						
NDELA	mg/Sm ³	<0.0001						
NMOR, NMEA, NPYR, NDEA, NPIP, NDPA, NDBA	mg/Sm ³	<0.0001						

To illustrate the difficulties in monitoring the quality of CO₂, data on impurities content as measured at TCM is given in Table 4. Two methodologies were used for the measurements: (i) online monitoring with gas chromatography (GC) and Fourier Transformed Infrared Spectroscopy (FTIR), and (ii) gas sampling and offline determination by an external lab using multiple methods (see Johnsen et al. 2018 for details).

The relative differences between online and manual measurements are high, particularly considering that the values measure for some of the components (e.g. ammonia, aldehydes, NOx) are in the same order of magnitude as the specifications considered.

A direct comparison between the two measurements for oxygen content determination is not possible, as the offline method gives the sum of oxygen and argon. We have estimated the amount of argon and subtracted it from the offline measurements. While this is not a precise calculation, it points at large discrepancies between the online and offline monitoring methods for oxygen content determination. More data would be required to determine which method is closer to the true O_2 content, and the difference is large enough so that in one case (online) there is no need for oxygen separation, whereas in the other case, there is.

While a large discrepancy is also observed for N_2 , this is of less concern as the measured values are in the 100s of ppm range, whereas specifications are in the vol% range. When separating oxygen in a CO_2 liquefaction plant, N_2 will also be separated (along with any other non-condensable). In contrast, if oxygen is combusted (catalytic oxidation), the nitrogen will remain in the final CO_2 product.

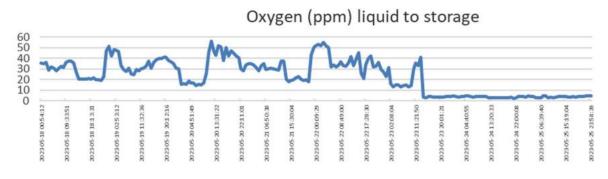


	21-0	6- 2017	9-11-2017			
	Online	Sampling	Online	Sampling		
Ammonia	2.2	1	6.1	3.4		
NO + NO ₂	Nd	Nd	Nd	0.5		
SO ₂	0.2	Nd	Nd	Nd		
Acetaldehyde	1.7	2.9	5.4	6.5		
Formaldehyde	0.3	Int	0.6	0.2		
N ₂	220	420	300	370		
02	1.8	40*	2	27*		
O ₂ +Ar		49		36		

Table 4. TCM data on impurities in raw CO₂: online monitoring vs. manual sampling. Source: Johnsen et al. 2018

*Value estimated based on calculated Ar content

In a recent report from the SCOPE project (ERA-ACT3), the quality of the liquified CO₂ produced at the Twence pilot plant was monitored by gas chromatography (online sampling). The data indicates that, while the oxygen content in CO₂ can be as high as 30-50 ppmv, optimizing the CO₂ stripper operation by increasing the CO₂ stripper boil-up ratio can lead to quite low O₂ content, meeting the more stringent specifications. This can be clearly seen in the 23rd, 24th and 25th of May data in Figure 1. Therefore, as long as the OCC systems are equipped with a liquefaction plant, which is the assumption here, it is likely that the inerts (non-volatile) content can be adequately controlled onboard.







6. Conclusions

OCC was demonstrated in EverLoNG onboard 2 vessels. In both campaigns, the impurities content in the exhaust gases and from the OCC capture pilot were monitored. The most relevant observation made in the context of CO_2 quality is the relatively high NOx content in the exhaust gas of marine engines. At TCM, the NOx content in the raw CO_2 is measured at 0.5 ppmv (Table 3), which is close to the Northern Lights and Aramis specifications. However, the reported NO₂ content in the flue gases of TCM is below 5 ppmv (Hume et al., 2022, Campbell et al., 2022), whereas in the EverLoNG campaigns values in the 50-250 ppmv range were measured. This indicates that the NOx content in OCC-produced CO_2 could potentially be higher than specifications.

There are different approaches to tackle this challenge. The first would be to (further) remove NOx from the exhaust gases, for instance by applying selective catalytic reduction (SCR) and/or separating NO₂ in the quench column by applying a sulphite-thiosulphate solution (this can also be integrated in a SOx scrubber). These add to the treating costs onboard, but has the benefit of protecting the amine-based solvent from NO₂-induced oxidative degradation.

Alternatively, and if the presence of relatively high NO_2 content in the liquid CO_2 wouldn't affect the onboard storage tanks, the on-shore CO_2 receiving terminals could be equipped with NOx separation technologies.

Future research should focus on: measuring the NOx content in the raw and liquid CO₂ in OCC pilots; verifying whether the risks of a potentially high NOx content is acceptable for the on-board storage tanks; evaluating and comparing different NOx removal technologies, from both technical and economic aspects. In the EverLoNG campaigns as well as in related literature, it was identified that the NO₂ leads to increased rate of oxidative degradation of solvents. This implies increased rate of formation of degradation products. Therefore, monitoring the presence of other impurities, in particular NH₃ and aldehydes in the raw and liquified CO₂ should also be a focus point in future research.



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