21GRD06 MetCCUS

Report A3.1.2: Literature survey on commercially available cylinders for the preparation of PRMs for CCUS

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Due date of the report: 31 March 2023

Actual submission date of the report: 20 June 2023

The project has received funding from the European Partnership on Metrology, co-financed by European Union Horizon Europe Research and Innovation Programme and from the Participating States.

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Summary

This report was written as part of activity A2.3.1 from the Partnership on Metrology project "Metrology for the support for Carbon Capture Utilisation and Storage" (MetCCUS). The three-year European project started 1st October 2022.

In the report, we have reviewed the surface passivation treatments that are available for gas cylinders for a number of impurities relevant for CCUS using information gained from literature review, experiences from partners, and other metrology projects in order to assess availability of cylinders that will allow stable mixtures to be produced. Most of the information is obtained from other matrices than CO_2. For some of these impurities, information is currently lacking. The outcomes of the project MetCCUS will allow to increase knowledge on appropriate gas cylinders by performing two-year stability study on defined mixtures.

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1 Introduction

Carbon capture, utilisation and storage (CCUS) refers to technologies that can play a role in meeting global energy and climate goals. Carbon capture with permanent storage (CCS) or utilization of the carbon dioxide (CCU) are effective tools to reduce CO_2 emissions [1] and contribute to reach climate goals set by the European Commission. New technologies for capturing CO_2 are developed, some methods are already applied to capture CO_2 from different sources. Many industries contributors to CO_2 emissions can use these technologies: cement plants, iron and steel plants, high-purity industrial sources such as natural gas processing, hydrogen production, coal/gas-to-liquids and ammonia production, pulp and paper industry, biofuels production etc. Depending on the source of carbon dioxide and the type of capture technology used, a certain quality of the CO_2 is generally required to guarantee process performance, components, health and safety. The document ISO/TR27291:2020 [2] describes the effects of the impurities present in the CO_2 stream on the storage (classified as physical, chemical, microbiological and toxicological). For example, impurities of the CO_2 stream can affect both the thermodynamic and transport properties (operating pressure, temperature, fluid density, safety considerations, fracture control and cloud dispersion). CO_2 can also be physically and chemically employed in the various fields of chemical, biological, and food processes [3]. Zhang *et al.* [4] recently reviewed the carbon dioxide utilization technologies including mineralization, biological utilization, food and beverage, energy storage and chemical production. As for any application, allowable levels (maximal limits) of certain impurities are needed to guarantee process performance, components, health and safety.

Analysing CO_2 composition with regards to impurities is critical to allow industry to accurately test the performance of new capture and utilization technologies to understand the degradation and purity of carbon dioxide and key impurities. Reliable analytical methods are needed to take decisions on CO_2 quality conformity against the required specifications.

Calibration of the instruments used in an analytical method has two objectives: to check the accuracy of the instrument and to determine the traceability of the measurement. A reference gas mixture, a mixture of gaseous components is used as a comparative reference in the calibration of gas analysers or gas detectors and as a means of establishing a known response to a certified chemical component concentration. Precision and accuracy of trace gas mole fractions depend among other factors on the stability of primary standards. Several studies in the past have documented instabilities of gas composition in high-pressure cylinders. These instabilities can either be viewed as temporal drifts of gas composition or as pressure-dependent composition changes along the lifetime of the cylinder gas [5].

The project “Metrology for the support for Carbon Capture Utilisation and Storage” (MetCCUS) aims among others at developing gas calibrants and reference materials needed by European laboratories to validate their analytical methods for CO_2 CCUS analysis. In this report, we review the surface passivation treatments that are available for gas cylinders for a number of impurities relevant for CCUS using information gained from literature review and other metrology in order to assess availability of cylinders that will allow stable mixtures to be produced.

2 Cylinders and passivation

Cylinders are made of different materials. The most common materials used today are aluminium, steel, alloys and composite materials.

Gases adsorb on many surfaces, in particular metal surfaces. There are two main forms responsible for these effects: physisorption and chemisorption [5]. Physisorption a process governed by low electrostatic interactions between the electron configuration of the adsorbate and the adsorbent, in particular van der Waals forces involving weak energy corresponding to 1–10 kJ mol−1 and therefore barely influences the electron structure of the substances involved, and mainly appears under low temperature conditions. Chemisorption involves much higher energies in the range of 100 to 1000 kJ mol−1 and often requires an activation energy, finally resulting in a structure that is similar to a chemical bond of either ionic or covalent type.

There are a multitude of different methods used to passivate the internal surface of cylinders. It exists a variety of treatment to fit different applications. The treatments are often to make the surface inert to targeted compounds, however as the treatment remain proprietary information, not a great deal of detail is known about these technologies [6]. Passivation is a technique used to occupy the active areas on the surface of a vessel.

Three categories of treatment can be distinguished:

1) Cleaning, polishing of the internal surface (electro) chemically or mechanically
2) Chemical treatment without targeting structural change of the surface
3) Multi-molecular layer coverage of the initial surface

Cylinders and available surface passivation treatments are reviewed for impurities listed in A3.1.1 (metals and particulates have been removed). The information presented has been obtained from literature (data is mostly available for gas standards in nitrogen and air), contact with cylinder´s providers, experience from participating NMIs, and other metrology projects (information in other matrix than CO_2 such as hydrogen, air and methane). Table 1 summarizes the results.

Impurities are classified as [7]:

– non-critical: no specific issues are expected, and many cylinders and most available treatments are expected to perform fine.

– critical: adsorption and/or stability issues expected

– very critical: reactive impurities

Table 1: Summary of candidate cylinders and treatments

component	CCUS Specifications Summary (NPL)	Classification	Canditate cylinders and treatments
water (H_2O)	≤20-50 ppm	critical	DB Gold Performance (Effectech [8]): NPL has reported stability for 5 ppm water in hydrogen. NPL says cylinders report slightly high, but due to the hydrophobic nature of the treatment may be a “truer” value due to lower adsorption losses Water was found to be stable at around 5 µmol/mol in hydrogen in SPECTRA-SEAL and SGS cylinders for a few months [9].
Sum [H_2+N_2+Ar+CH_4+CO+O_2]			
H_2	≤0.005-2%	non-critical	Experiments performed on aluminium and steel cylinders demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO_2 (~400 ppm), CO (10-200 ppb), CH4 (~2 ppm), and H2O (1-30 ppm) than steel cylinders
N_2	≤1-4%	non-critical	
Ar	≤1-4%	non-critical	Concentration changes of CO in aluminum cylinders from 0.1 to 0.5 % depending on time (0.1 % for 6 months, 0.3 % for 12 months, 0.4 for 18 months, 0.5 % for 24 months). Mixtures were prepared in concentration range from 100 ppm to 1000 ppm. [10]
CH_4	≤1-4%	non-critical	
CO	≤0.01-0.2%	non-critical	
O_2	≤10-20 ppm	very critical	
total sulfur-contained compounds (incl. mercaptan)	≤20 ppm	very critical	Should perform as for H_2S
COS	≤20 ppm	very critical	Stability of COS would be similar to that of H2S within the DB gold effectech cylinders
DMS	≤20 ppm	very critical	DMS PRMs are projected to be stable for 9~12 years in aluminum cylinders with Performax, Aculife, and Experis surface treatments while, without the special surface treatments, the stability varies from 1.5 years to 3.5 years. [11] KRISS has developed DMS standards in Al-Experis cylinders, The DMS in the Al-Experis cylinder was projected to be stable for more than 4 years within an uncertainty of 3% [12]
H_2S	≤5-20 ppm	very critical	DB Gold Performance (Effectech [8]): NPL has tested multisulphur mixtures at 5ppb in hydrogen as part of MetroHyve II. Coating performed well. IPQ uses cylinders with the special treatments Aculife III and IV and Megalife (Scott Specialty Gases).

SO_x	≤10-100 ppm	very critical	Spectra-seal cylinders IPQ uses cylinders with the special treatments Aculife III and IV and Megalife (Scott Specialty Gases). Aluminum cylinders should be suitable for SO2 according to review at the concentration from 9 to 100 ppm. Maximum change of the concentration 1 % in 24 month [13, 10]
Total NO_x	NO_x: ≤10-100 ppm	very critical	NO2 in general is quite unstable instability will have little to do with the passivation treatment. NPL prepares NO2 mixtures with an excess of oxygen to prevent instability, in Spectraseal coated cylinders, at 10ppm NPL can only guarantee about a year's stability Within framework of MetNO2 project, NO2 were prepared in Aluminum cylinders (sausage type) with a SilcoNert 2000 coating. See table 2 below for other options IPQ uses cylinders with the special treatments Aculife III and IV and Megalife (Scott Specialty Gases). Concentration change of NO2 in aluminum cylinders should be lower than 1 % at concentration 100 ppm. [13]
Total aliphatic hydrocarbons (C2 to C10)	≤1.15-6%	non-critical	aluminum cylinders internally passivated with either Spectraseal (BOC) or Experis (Air Products) treatments [12]
Total aromatic hydrocarbons (C6 to C10, incl. BTEX)	≤15 ppm	non-critical	Aluminum cylinders internally passivated with either Spectraseal (BOC) or Experis (Air Products) treatments [12] NPL uses Experis coated cylinders (according to their experience, perform better than Spectraseal) NPL has tested DB Gold cylinders with a 30 component Ozone precursor mixture in nitrogen at 4 ppb. All were shown to be stable for a month. The components in the list were: ethane, ethene, propane, propene, i-butane, n-butane, ethyne, trans-2-butene, 1-butene, cis-2-butene, i-pentane, n-pentane, 1,3-butadiene, trans-2- pentene, 1-pentene, 2-methylpentane, n-hexane, isoprene, n-heptane, benzene, 2,2,4-trimethylpentane, n-octane, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzeneand 1,2,3-trimethylbenzene.
Total volatile organic compounds (excl. methane, total aliphatic HC (C2 to C10), methanol, ethanol, and aldehydes)	≤20-60 ppm	non-critical	See above
Total aldehyde compounds		critical	Formaldehyde in nitrogen at nominal 2 ppm [12]. Al-Acu-VIII cylinders appears to be suitable for use with formaldehyde in nitrogen mixtures, with a relative loss rate of <1% yr−1 or 1.2% a year, slow linear loss over 1 year (about 0.7% per month) in Luxfer (10L, SGS)

			10 ppm in N_2 in Spectraseal (10L, BOC): calculated decay rate of 1.6 ppb a day [14] [15] Experiments with Silconert 2000, Sulfinert and Performax showed with more than 80 % stability over 1 month at 1 µmol/mol formaldehyde in hydrogen [7].
Ethanol		critical	Ethanol tends to adsorb to cylinder inner wall Based on CCQM-k93 report: Scott (Aculife IV) cylinders was mostly used for ethanol in nitrogen [16].
Methanol		probably non-critical	
Hydrogen cyanide (HCN)		?	
Total amine compounds	≤0.08-10 ppm	?	
Total glycol compounds	≤0.025-0.05 ppm	?	
Ammonia (NH_3)	≤10-1500 ppm	critical	10 ppm and 100 ppm NH_3 mixtures in nitrogen [17]. No losses were observed with SilcoNert 2000 coated cylinders, relatively good performance for Spectraseal cylinders (BOC Linde) and cylinders from Takachiho. 10 ppm in nitrogen was found stable in Aluminium SPectraseal (10 L, BOC), Aculife IV (Air Liquide), Takchiho, Stainless steel Silconert 2000 (1 L, Restek) for 12 month within 3% uncertainty [18] Significant initial loss (>50%) were observed for NH3 at 0.2 ppm in hydrogen in Spectraseal (10 L, BOC) and Luxfer (10 L, SGS) [19]
Total carboxylic acid and amide compounds		?	
Total phosphorus-contained compounds		?	
Ethylene (C_2H_4)		Non-critical	
Acid forming compounds	≤10-70 ppm	Very critical	
Nitrosamines and nitramines		?	
Dioxins and furans		?	

Additional information on NO_2

Table 2 gives an overview of the cylinders tested within the framework of the MetNO2 project and the performance as assessed by the partner.

Table 2: assessment of cylinder performance for NO2 obtained within the framework of MetNO2 [20]

Passivation	Manufacturer	Material	Water volume (L)	Partner	Observed stability	Observed NOy	Performance*	Remarks
Alpha Tech (Air Liquide)	Luxfer	Aluminium	5 and 10	VSL	Good	~ 1%	Good	-
SilconNert 2000	Swagelok	Stainless steel	3.6	VSL	Reasonable	High (up to 5%)	Bad	Probably valves are not suitable for NO2 gas mixtures due to higher leak rate
Aculife III (Scott)	Luxfer	Aluminium	5	TUBITAK	Good	-	Good	Aculife III-IV (Scott)
Experis (TC1 – chemical treatment)	Luxfer (Air products)	Aluminium	10	LNE	Reasonable for NO2 in N2, bad for NO2 in air	-	Reasonable for NO2 in N2, bad for NO2 in air	Formation of HNO3
NO2 treatment (4 bar)	Luxfer (Air Liquide)	Aluminium	11	LNE	Reasonable for NO2 in N2, bad for NO2 in air	-	~ 1%Reasonable for NO2 in N2, bad for NO2 in air	Formation of HNO3
Spectraseal (BOC)	Luxfer	Aluminium	10	NPL	Reasonable	~ 1%	Reasonable	Variable amounts of NOy observed
Megalife (Air Liquide)	Luxfer	Aluminium	10	NPL	Reasonable	~ 0.5%	Reasonable	More consistent amounts of Noy observed

3 Conclusions

CO_2 composition assessment with regards to impurities is critical to allow industry to accurately test the performance of new capture and utilization technologies to understand the degradation and purity of carbon dioxide and key impurities. Reference gas mixtures are needed to calibrate analytical instruments used for this assessment. The method´s precision and accuracy depend directly on the stability of primary standards. Several studies in the past have documented instabilities of gas composition in high-pressure cylinders. Cylinders are made of different materials. The most common materials used today are aluminium, steel, alloys and composite materials. There are also a multitude of different methods used to passivate the internal surface of cylinders to make the surface inert to targeted compound. Cylinders and available surface passivation treatments have been reviewed for impurities relevant for CCUS processes. The information presented has been obtained from literature (mostly for gas standards in nitrogen and air), contact with cylinder´s providers, experience from participating NMIs, and other metrology projects. The report clearly shows some gaps in knowledge for appropriate cylinders and treatments. The outcome of MetCCUS will contribute to increase this knowledge.

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