Potential Measurement Issues relating to Corrosive, Waste, Incidental or Trace Substances in CO2 Streams destined for Geological Storage: Initial Report

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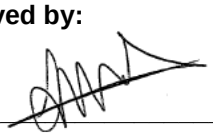

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1. Introduction

1.1 Intended readership

This report is mainly intended for organisations concerned with the regulation of, generation, storage and analysis of carbon dioxide streams destined for geological storage.

1.2 Scope

This report covers the potential analytical measurement issues which need to be considered for carbon dioxide streams which are intended for geological storage. There are a wide range of potential contaminants and other trace compounds in these CO_2 streams, arising from different sources of CO_2 which are capable of promoting different physico-chemical effects during introduction and storage.

1.3 Background

The storage of carbon dioxide in both secure underground and under-sea geological formations such as depleted oil and gas reserves is becoming a more favoured approach for reducing carbon dioxide emissions into the atmosphere as a response to the problem of global warming. The storage created for these carbon dioxide streams is intended to be permanent. This process is generally known as Carbon capture and storage or Carbon capture and sequestration, CCS for short. The UK Government is actively looking at partners for demonstration projects to highlight the technology and opportunities in the UK. Although a proposed CCS project at Longannet in Fife, Scotland[1], will not now proceed with funding from the Department of Energy and Climate Change (DECC), other opportunities have already been identified which could be taken forward, which include one at Peterhead, Scotland[2], and another at Ferrybridge, Yorkshire[3]. CCS technology has already been demonstrated in the USA[4] and in other EU countries[5].

Although the major risks associated with CCS are from leakage of the stored CO_2, and accidents arising from the injection of CO_2 under pressure into the geological storage site, there may be other risks arising from the nature and concentration of contaminants in the CO_2 stream, although these have been much less widely reported or studied[6]. The technology applied to CCS is relatively young, and the volume of information relating to measurements of contaminants in CO_2 streams and problems arising from these contaminants is limited. There have been limited developments on CCS in the United Kingdom.

[1] DECC Press Notice 11/84: Government reaffirms commitment to CCS - Department of Energy and Climate Change
[2] The Guardian, 9 November 2011: Energy companies join forces for UK's first carbon-capture project | Environment | guardian.co.uk
[3] DECC Press Notice 11/103: Chris Huhne opens UK's first Carbon Capture plant - Department of Energy and Climate Change
[4] National Mining Association (USA): CCS Projects
[5] EU Energy Commission: Energy: CCS Project Network - European commission
[6] A carbon capture and storage network for Yorkshire and Humber, report by Yorkshire Forward, page 14: http://www.co2sense.co.uk/uploads/public/CCS%20Network.pdf

2. Contaminants and their Sources in CO_2 streams

2.1 Contaminants and Impurities

The identity and quantity of contaminants in CO_2 streams destined for geological storage depends on the source of the CO_2. Different industrial processes give rise to a different contaminant profile.

The majority of current and projected applications of CCS technology relate to emissions from power stations which burn fossil fuels[7]. Other industrial processes which could be considered amenable to CCS technology include:

- Cement and Lime production
- Fermentation to produce ethanol
- Iron and steel production
- Ammonia production
- Hydrogen production

The contaminants which can be found in CO_2 streams from these sources include:

- Water
- Oxides of Nitrogen (NO_x)
- Oxides of Sulfur (SO_x)
- Methane (CH_4) and other short-chain hydrocarbons
- Hydrogen sulphide (H_2S)
- Argon
- Nitrogen
- Carbon Monoxide (CO)
- Oxygen
- Chlorine
- Ammonia (NH_3) and volatile amines
- Toxic metals (Hg, As, Se)

2.2 Effects of Contamination

CCS technology therefore needs to guard against levels of one or more of these contaminants which could adversely affect the integrity of the storage site or the relevant transport infrastructure (corrosion and impact on fluid characteristics), which do not pose a significant risk to the environment and human health, and do not breach applicable UK or EU legislation. This would normally be achieved by clean-up of the CO_2 stream prior to injection into geological storage.

For example, the presence of water in the CO_2 stream at an elevated level can produce acidic conditions with the CO_2 which could cause corrosion of the pipe

[7] CO_2 Capture Project Consortium (CCP): Regulatory Treatment of CO2 Impurities for CCS Report (2007)

through which the stream is travelling[8]. A limit of 500 ppm water is therefore recommended as postulated in the Dynamis project (EU 6th Framework Project, 019672)[9].

Hydrogen sulfide can also present problems in storage, particularly in acidic conditions, even mildly acidic conditions. In such situations, iron can be removed as iron sulfide from rocks, which may influence the integrity of the storage area[10].

Contaminants in CO_2 streams can also have an effect on the physico-chemical properties of the stream, including density, viscosity and interfacial tension[11]. Variations in these properties can affect the interaction between the CO_2 stream and the reservoir boundaries.

The exact identity and concentration of impurities in CO_2 streams is dependent on the individual emission source. Compositions vary both within generic source types, and can be affected by factors such as the fuel or other process material, the process and the processing plant. Therefore, although the type of facility producing the emission can indicate the generic composition of the stream, and the likely impurities, only analysis of the stream can give the detailed information necessary to fully understand the potential effects on the integrity of the storage.

3. Analytical Methodologies for Contaminants in CO_2 streams

The development of measurement methodology for the determination of contaminants in CO_2 streams is still relatively young, and there is very little information available to indicate how these measurements have been, or can be, made. Much of the work into studying these CO_2 streams has concentrated on how to trap the CO_2 from the gas emission source and how the streams behave physically during injection into, and subsequent storage in, the geological site.

3.1 Gaseous Impurities and Contaminants

There are many documented procedures for the determination of gas mixtures which could be applied to CO_2 streams, although none appear to have been applied in this area to date. Separation and quantification of gases which include carbon dioxide and gaseous contaminants in CO_2 streams is normally carried out by gas chromatography using a solid-phase column such as Porapak or Haysep, and detection using either a flame ionization detector (FID), a thermal conductivity detector (TCD), a flame photometric detector (FPD) or a sulfur chemiluminescence detector (SCD) for sulfur-containing gases, or a discharge ionization detector (DID). Although there are few published methods for the direct determination of gaseous contaminants by gas chromatography, methods have been published relating to nitrogen oxides[12] (also relates to sulfur dioxide), sulfur-containing gases[13] (hydrogen sulfide, sulfur dioxide), methane (and other

[8] Implementation of Directive 2009/31/EC on the Geological Storage of Carbon Dioxide Guidance Document 2: Characterisation of the Storage Complex, CO2 Stream - Composition, Monitoring and Corrective Measures, European Commission, 2011, ISBN-13 978-92-79-19834-2:
[9] Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage (Dynamis Project): D 3.1.3 CO_2 quality recommendations, June 2007
[10] Presentation to 1st International Oxyfuel Combustion Conference, Cottbus, September 2009
[11] GV Last and MT Schmick, Identification and Selection of Major Carbon Dioxide Stream Compositions, Report for US Department of Energy, Contract PNN-20493.
[12] Environmental Protection Agency Subchapter C – Air Programs Part 60 Appendix A to Part 60 – Test Methods 40 CFR 60. Appendix A to Part 60
[13] South Coast Air Quality Management District, Applied Science & Technology Division, Laboratory Services Branch, SCAQMD Method 307-91: http://www.aqmd.gov/tao/methods/lab/307-91.pdf

short-chain hydrocarbons)[14], and water[15]. Water is also commonly measured in gas streams using oxide capacitance and electrolysis instruments[16]. Oxide capacitance instruments have the advantage that they can determine moisture over a wider range, whereas electrolysis instruments are generally effective at very low water contents, i.e. below 10 mg/kg.

One industry which has a need for measuring gaseous impurities in bulk quantities of carbon dioxide is the beverage industry. The International Society of Beverage Technologists (IBST) have a number of analytical procedures for measuring impurities in CO_2 streams which are described in ISBT Manuals available from the ISBT website at www.bevtech.com. Species which are measured using these procedures include moisture (0 - 100 mg/kg), oxygen (0 - 30 mg/kg), ammonia (0 – 10 mg/kg), oxides of nitrogen (0.2 - 10 mg/kg), methane (0 -100 mg/kg), sulfur dioxide (0.02 – 2 mg/kg) and total sulfur (0 – 1 mg/kg).

It has not been possible to find any methods relating to the determination of ammonia and/or other volatile amines in appropriate matrices which could be applicable to their measurement in CO_2 streams.

3.2 Trace Metals

Similarly, there are many methods for the determination of trace metal contaminants which could be potentially applied to CO_2 streams including atomic absorption spectroscopy (AAS), inductively-coupled plasma optical emission spectrometry (ICP-OES) and inductively-coupled plasma mass spectroscopy (ICP-MS). These could be utilized to determine trace metals following separation by, for example, absorption from the flowing gas stream on to a filter. Quantitation can then be achieved providing the gas flow, the absorption time and the filter area were accurately known.

Developments have recently been made[17] at the University of Sheffield to monitor trace elements in continuous gas streams, which could potentially be applied to CO_2 streams, by direct multi-element monitoring by ICP-OES.

4. Conclusions

Carbon capture and sequestration is in its relative infancy, and few projects have been undertaken to capture and store carbon dioxide in geological storage. A number of contaminants have been identified which can be found in these streams, depending on their source. The potential problems which undesirable levels of these contaminants, particularly water, can cause are also well understood.

There does not appear to be any specific analytical methods for determining these impurities in CO_2 streams, although chromatographic methods for separating and measuring gaseous impurities can be used, and absorption of trace metal impurities for subsequent determination by techniques such as ICP-MS and ICP-OES, or direct determination in flowing gas streams, are also feasible.

[14] Tipler A, Perkin Elmer Gas Chromatography Application Note (2001): http://www.perkinelmer.com/CMSResources/Images/44-130319APP_HydrocarbonsinGasStreamsSwafer.pdf
[15] Andrawes FF, Anal. Chem., 1983, 55 (12), pp 1869–1872
[16] Downie NA, Industrial Gases, Chapman & Hall (publ) (1997), pp183-184.
[17] Sheffield University Mobile Emissions Laboratory: SUWIC

Further work on developing and validating methodology for determining impurities in CO_2 streams is needed in order to accurately measure these contaminants to ensure they are not at a level where they can cause future problems. A limited study could be carried out at LGC on the development of methodology for the determination of some of the gaseous contaminants listed by gas chromatography as part of this activity.

5. Acknowledgements

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