CHALLENGES AND OPPORTUNITES OF ACHIEVING EUROPEAN CO_2 TRANSPORTATION AND STORAGE SPECIFICATIONS FOR CARBON CAPTURE IN THE IRON AND STEEL INDUSTRY

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Abstract

The application of CCS in the iron and steel industry faces particular challenges for achieving European CO_2 transportation and storage in meeting CO_2 stream impurity limit specifications due to the unique and diverse composition of the steelworks off-gases targeted for CO_2 capture and the separation efficiency of proposed CO_2 capture solutions. This paper reviews the range and levels of compounds that could form potential CO_2 impurities in steelworks off-gases and provides estimates of the quality of CO_2 products obtained in primary CO_2 capture steps from Blast Furnace Gas (BFG) using different technologies of Pressure-Swing Adsorption (PSA) and amine scrubbing. Published CO_2 specifications from European transportation and storage operators are reviewed and compared. Additional suitable purification steps that are needed in order to reduce the levels of impurities from primary CO_2 product streams in order to achieve European CO_2 impurity limit specifications are identified, characterised and the associated cost implications discussed.

Keywords: CCS, CO₂ Quality, Iron & Steel, Impurities, CO₂ Purification

1. Introduction

The iron and steel industry represents the largest energy consuming manufacturing sector in the world, with average specific emissions being around 1.83 tonnes of CO_2 per tonne of all crude steel produced and global crude steel production reaching 1.86 Gt for the year 2020. The CO_2 footprint of steel mills accounts for up to 8% of anthropogenic emissions.

A unique feature of the current steel making processes is the presence of energy containing off-gases, with the three main being Coke Oven Gas (COG), Blast Furnace Gas (BFG) and Basic Oxygen Furnace Gas (BOFG). Conventionally, these off-gases are used to fuel reheating furnaces or for power generation, but are increasingly now targets for the application of Carbon Capture and Storage (CCS). CO_2 capture strategies for steelworks off-gas application aim to separate CO_2 while producing another energy containing gas stream for further use with much reduced carbon content. The general characteristics of the steelworks off-gases are shown in table 1. COG is the most energy rich of these streams containing ~65 vol% H_2 while the BOFG has significant CO content (>50 vol%). BFG represents the greatest volumetric flow, and is hence the focus of particular attention for CCS

application, but has a low energy content, consisting of ~50-60 vol% N_2 and ~20 vol% CO_2.

Table 1: Main components and characteristics of steelworks off-gases **Error! Reference source not found.**.

Component	mol%		
	COG	BFG	BOFG
Carbon monoxide (CO)	3.8	22.3	56.9
Carbon dioxide (CO_2)	0.96	22.1	14.4
Hydrogen (H_2)	59.5	3.6	2.4
Nitrogen (N_2)	5.8	48.8	13.8
Ethane (C_2H_6)	2.7	0.0	0.0
Methane (CH_4)	23.0	0.0	0.0
Oxygen (O_2)	0.2	0.0	0.0
Water (H_2O)	4.0	3.2	12.2
Lower Heating Value (LHV) (MJ/Nm^3)	17.8	3.3	8.5
Flowrate (kg/s)	0.3	158.7	14.2

The fate of the main steelworks off-gas components and a range of other contaminants when CCS systems are applied, and the degree to which these will carry over into CO_2 product streams to form impurity compounds, is an important issue for the iron and steel industry. Impurities also need to be accounted for when capturing CO_2 from many other emitting industries (e.g. cement, waste-to

energy, refineries etc.). This is because the anticipated impurities can have a range of mainly deleterious impacts on different parts of the CCS chain (i.e. on the capture process and compression/liquefaction equipment, CO_2 transportation infrastructure (pipeline and/or ship tanker), CO_2 injection well and geological storage sites). These impurity impacts include toxic effects on humans, corrosion effects on metals, metal embrittlement, along with effects on hydraulic efficiency, pipeline fracture behaviour, geological storage capacity and geochemistry (e.g. mineral dissolution and precipitation). CO_2 impurity impacts have received attention from the CCS scientific community [2][3], with some operational experience gained from CO_2 Enhanced Oil Recovery (EOR) [4]. The CO_2QUEST project [5] reviewed typical compositions of CO_2 streams from CCS and provided experimental results for the effect of impurities on pipeline rupture and CO_2 dispersion behaviour using extensively instrumented realistic-scale pipeline test facilities. Experimental and modelling results for the geological impact of impure CO_2 were also obtained while full-chain CCS techno-economic tools were developed.

In view of the impacts of CO_2 impurities, CO_2 transportation and storage providers set concentration limits for impurities, meanwhile other authors propose to determine CO_2 stream composition based on a case specific multi-criteria optimisation. Despite a significant body of knowledge acquired, the fate and impact of impurities in CCS still requires an improved understanding and characterisation in order to facilitate technology roll-out, especially in consideration of the widening scope of applications and development of future generations of CO_2 capture technologies. Research is also needed on the associated cost benefit analysis of CO_2 purification while simultaneously considering the operational and safety aspects surrounding the potential for co-transportation/-storage of CO_2 impurities.

In this paper, the range and level of impurities in steelworks off-gases are reviewed and the propensity of components to form impurities in the product streams from different primary CO_2 capture steps, including Pressure-Swing Adsorption (PSA) and amine based systems, is assessed. Following a review of current European CO_2 stream transportation and storage specifications, the requirements for the application of additional CO_2 stream clean-up technologies are identified and assessed.

2. Potential impurities in steelworks off-gases

The application of CCS to steelworks off-gases can result in new challenges due to the presence of a high number of different impurities as compared to other industrial emitters which use natural gas as a feedstock or fuel. In addition to the main components listed in table 1, other impurities may be present in low concentrations (in the parts per million (ppm) or parts per billion (ppb) region). The main compounds and their categories have been summarised by Schittkowski et al. [6] and are shown in table 2. Some of these compounds have known toxic effects on humans (e.g. mercury (Hg)) while others pose corrosion concerns to metals, especially when present in mixtures with water (e.g. hydrogen sulfide (H_2S), which is also poisonous and flammable, and sulfur oxides (SO_x)).

Table 2: Potential impurities of exhaust gases from steel production [6].

Compound class	Compound
Hydrocarbons	CH_4, C_2H_4, C_2H_6, cyclopentadiene, C_3H_8, C_3H_6, C_4H_{10}, acetylene, pentene, heavy hydrocarbons
Aromatics	Phenol, benzene, toluene, xylene
PAH	Naphthalene, phenanthrene, benzopyrene,
S-compounds	SO_x (SO_2), H_2S, COS, CS_2, thiophene, mercaptan
N-compounds	NO_x (NO_2, NO), NH_3, HCN, tar bases (C_xH_yN), pyridine, $(CN)_2$
O-compounds	O_2, H_2O, tar acids (C_xH_yOH)
Heavy metal compounds	Cr, Mn, Ni, Pb, Zn, Hg, As, Cd, Cu
Halides	HCl, HF, inorganic flourides, PCDD/F, PCB
P-compounds	Trivalent phosphorus
Dust	FeO_x, alkali metals, alkali earth metals, metal oxides, CdO_x, elemental sulfur, elemental carbon, Hg

PAH: Poly aromatic hydrocarbon;
PCCD/F: Polychlorinated benzo(p)dioxin and furan.

A small number of literature resources give details of the concentration levels of impurity compounds in steelworks off-gases. The most comprehensive of these, which also includes the state-of-the art in the purification of steelworks off-gases, is the European Commission (EC) document "*Best Available Techniques (BAT) Reference Document for Iron and Steel Production*" [7]. Levels of impurity compounds in steelworks off-gases vary in different plants depending on a variety of considerations including the age of the plant and operational factors, such as the degree of pollution removal technologies employed and the type of coal selected for coke production (e.g. low or high sulfur coal). Table 3 shows the concentrations of some impurity compounds reported in [7]. BFG is known to contain different levels of H_2S; 14 mg/Nm^3 given in table 3 is equivalent to 10 ppm_v which is in the lower range of other reported ranges. For example, Bender et al [8] report H_2S to be present in BFG in the range of 10-40 mg/m^3. More recently, Lanzerstorfer et al. [9] measured a range of gaseous components in BFG emissions and characterised the top scrubber efficiency; they found that the clean gas emission of sulfur was dominated by carbonyl sulfide COS (at 279 mg/m^3 (standard temperature and pressure - STP)) which accounted for about 85% of the total sulfur emissions, while H_2S and SO_2 accounted only for 15% and 0.6%, respectively. Although no data is available in the EC BAT document, the nitrogen containing species, HCN and NH_3 are believed to be present in BFG, but levels in the clean gas are believed to be low at 0.12 and 0.15 mg/m^3 (STP), respectively, according to the recent measurements [9]. Low levels of heavy metals Mn, Pb and Zn are also reported for BFG in table 3. Compounds other than those reported for BFG in table 3 may be

Table 3: Concentration levels of some potential steelworks off-gas impurities [7][11].

	BFG		COG (untreated)		BOFG	
	Concentration	Unit	Concentration	Unit	Concentration	Unit
Particulates	1-10	[mg/Nm³]	-	-	15-20	g/t LS
H_2S	14	[mg/Nm³]	20-700	[mg/Nm³]	-	-
Organic sulfur	-	-	≤ 150	[mg/Nm³]	-	-
NO_x	-	-	-	-	5-20	g/t LS
HCN	n/a	[mg/Nm³]	0.3-1.5	[g/Nm³]	-	-
NH_3	n/a	[mg/Nm³]	50-100	[mg/Nm³]	-	-
Heavy metals:						
Mn	0.1-0.29	[mg/Nm³]	-	-	<0.01-1.2	g/t LS
Pb	0.01-0.17	[mg/Nm³]	-	-	0.13-0.9	g/t LS
Zn	0.03-0.17	[mg/Nm³]	-	-	-	-
Cr	-	-	-	-	0.01-0.36	g/t LS
Cu	-	-	-	-	0.01-0.04	g/t LS
BTX	-	-	1-10	[g/Nm³]	-	-
Naphthalene ($C_{10}H_8$)	-	-	200-500	[mg/Nm³]	-	-
Tar	-	-	20-31	[mg/Nm³]	-	-
PAH	-	-	-	-	0.08-0.16	mg/t LS
PCCD/F	-	-	-	-	<0.001-0.06	µg I-TEQ/t LS

n/a: data not available; LS: (crude) Liquid Steel; BTX: Benzene, Toluene and xylene isomer;

present such as O_2 and CH_4, in addition to low levels of HCl, BTX and other smaller hydrocarbons. It is also worth noting that large time-dependent fluctuations in the compound concentrations may occur during steelworks operations [10], hence the presented values may be considered as average. As also shown in table 3, COG can contain some similar inorganic compounds as BFG (i.e. sulfur compounds, NH_3, HCN), and typically contains a wide range of light and heavy hydrocarbons. COG is typically cleaned before being used as fuel in a steel plant, to remove dust, tar, naphthalene, light oil, sulfurous compounds and the cracking of ammonia to hydrogen [11]. BOFG is known to contain levels of dust and NO_x, as well as low levels heavy metals (Mn, Pb, Cr, Cu), PAH and very low amounts of PCCD/F.
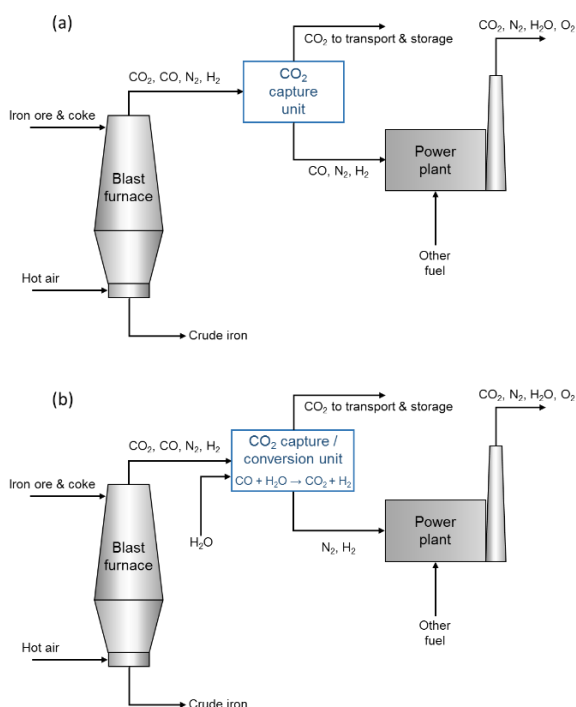
3. Impurities in CO₂ streams produced by capture from BFG

For a better understanding of the implications of impurities present in steelworks off-gases on CCS systems, estimates have been made of their levels in CO_2 streams captured from BFG using a mass balance technique applied to a generic CO_2 capture scheme shown in figure 1(a). Figure 1(b) also shows the case for a CO_2 capture and conversion process which can be achieved using technologies such as Sorption Enhanced Water Gas Shift (SEWGS) [1] or Calcium Assisted Steel-mill Off-gas Hydrogen (CASOH) technologies [12].

Table 4: Main impurities in CO₂ captured from BFG using PSA and amine systems estimated in this work.

	PSA low purity	PSA high purity	MEA plant
CO_2 mol% dry	83	99.5	99.7
H_2O mol%	saturated	saturated	saturated
N_2 mol% dry	10.57	0.29	0.023
CO -	5.27%	0.15%	200 ppmᵥ
H_2 -	0.96%	266 ppmᵥ	214 ppmᵥ
COS ppmᵥ	163	214	131
H_2S ppmᵥ	50.8	66.9	41
SO_2 ppmᵥ	1.1	1.4	0.9
HCN ppmᵥ	0.02	0.001	0.45
NH_3 ppmᵥ	0.05	0.0007	0.88
HCl ppmᵥ	0.04	0.001	0.71
Amine ppmᵥ	-	-	<1

Table 4 provides the estimated concentrations of major impurities for two different CO_2 capture technologies that are considered here: PSA and amine based systems. The performance of the PSA system is based on that reported during pilot scale trials in the COURSE50 project using the Zeolum F-9H sorbent, in terms of CO_2 purity and recovery rates achieved [13]. Two PSA cases are presented comprising a low purity case, based on a CO_2 purity of 83 mol% and recovery of 67%, and a high purity case based on 99.5 mol% purity and 61% recovery.

Figure 1: Simplified process schemes for (a) CO₂ capture and (b) CO₂ capture / conversion from BFG.

Based on the typical behaviour of PSA systems, the sulfur species (i.e. COS, H_2S and SO_2) are assumed to enrich in the CO_2 product (adsorbate) and therefore partition completely. All other species are assumed to distribute evenly between the non-CO_2 portion of the CO_2 rich stream and the CO_2 lean streams exiting the PSA system since they have lower molecular weights. It should be noted that in the pilot-scale system testing [13], a desulfurisation unit was included prior to the PSA system, whereas this stage is neglected in the current analysis. The estimation of the CO_2 composition captured from BFG using an amine system is based on the laboratory based analysis reported by Dreillard et al [14] for monoethanolamine (MEA) and DMX solvents, which achieved CO_2 purity set at 99.7 mol% (dry basis) and a CO_2 capture rate of 90%. The concentration of CO was reported to be 375 ppm$_v$ in the stripper top in the case of capture using MEA applied to an inlet gas representative of Top Gas Recycling (TGR) conditions with a composition of CO_2=37.04 mol%, CO=46.71 mol%, N_2=9.21 mol%, H_2=7.04 mol%, hence the value used in table 4 is proportionally scaled to account for the lower inlet concentration of CO in the typical BFG case. The concentration of amine in the CO_2 product is also based on the reported value by Dreillard et al for the TGR case. In the MEA case, sulfur containing compounds, nitrogen containing contaminants (NH_3 and HCN) and HCl are all assumed to partition completely with CO_2. HCN and SO_2 may form heat stable salts and COS may also undergo hydrolysis in amine systems [15]. The values presented here for the MEA case may therefore represent conservatively high estimates for contaminant concentration and actual values require a thorough investigation through experimental measurement.

4. European specifications for CO₂ transport and storage

Three European specifications for CO_2 transportation and storage have recently been published from the Northern Lights CCS project [16], National Grid in the UK [17] and TAQA for the PORTHOS project [18]. The Northern Lights project is part of the Norwegian full-scale CCS project, which includes the capture of CO_2 from industrial sources beginning in the Oslofjord region; the CO_2 will be liquified and shipped to a Northern Lights facility near Bergen, where it will be pumped 2,600 meters below the sea floor into a saline aquifer. The National Grid CO_2 specification has been developed since 2009 in the context of the UK Government's CCS commercialization competitions and has been based largely on the specification provided by the DYNAMIS consortium, with some adjustments for some compounds such as H_2S to ensure the pipelines do not become classed as "*sour service*" and the water level to prevent material degradation. The PORTHOS project associated to TAQA's CO_2 specification, will use depleted gas fields in the North Sea to store CO_2 which will be captured from industrial emitters in the Port of Rotterdam area and transported by pipelines. Table 5 shows the CO_2 specification provided in these three resources. For the

comprehensive breakdown of the rationale behind the proposed limits for each component in the three specifications, the reader is referred to the relevant reports [16][17][18].

Comparing the different specifications, it can be seen from table 5 that similarities and differences exist. TAQA's specification is the most comprehensive with precise recommendations provided for 21 components. The Northern Lights specification provides recommendation for amine and potential degradation products (NH_3, formaldehyde, acetaldehyde) and, generally sets the most stringent limits on all components barring NO_x, H_2S and HCN. The National Grid minimum concentration for CO_2 is 96% for dense phase CO_2 which is broadly in-line with the TAQA recommendation where the sum of non-condensable components must not exceed 4 vol%. No specific lower limit is set for CO_2 in the Northern Lights specification but non-condensables will be limited by their solubility in liquid CO_2 during interim storage. In all three specifications, tight limits are set for H_2O (30-50 ppm$_v$) and O_2 (10-40 ppm$_v$), while limits for NO_x range from 5 to 100 ppm$_v$. Some variation is observed between the three specifications in the case of sulfur species; TAQA's limit for H_2S is lowest at 5 ppm$_v$, followed by the 10 ppm$_v$ limit for Northern Lights and 80 ppm$_v$ gas and the 20 ppm$_v$ dense phase National Grid limits. These H_2S limits are in contrast to the composition of transported CO_2 in North America for the purposes of EOR in the Weyburn Project, where around 0.9 vol% H_2S is co-injected into an oil reservoir. H_2S is known to have a beneficial effect for EOR due to the reduction of the minimum miscibility pressure for CO_2 and oil mixtures, while a range of other factors such as population density are considered to account for differences in the limits on H_2S between North American and European CO_2 transportation and storage applications. National Grid's limit on H_2S was selected to avoid selection of pipeline materials for sour service. Variation in the permitted concentrations of SO_x is also observed between specifications with Northern Lights being the lowest at 10 ppm$_v$ and National Grid having the highest at 100 ppm$_v$. Only TAQA gives specific low limits for COS (at 0.1 ppm$_v$) and $(CH_3)_2S$ (at 1.1 ppm$_v$). A large disparity on the limits for hydrogen is observed with a limit of 50 ppm$_v$ imposed in the case of Northern Lights but much higher tolerances for National Grid at 2 vol% and TAQA at 0.75 vol%. A notable disparity also exists in the case of CO where at National Grid and TAQA allow up to 2000 and 750 ppm$_v$, respectively, but Northern lights has the tightest restriction at 100 ppm$_v$.

Given the types and levels of impurities expected in CO_2 streams captured from BFG presented in table 4 and the limits imposed for impurities in the CO_2 specifications of table 5, insights can be gleaned into which components may be problematic for the iron and steel industry in meeting the CO_2 purity requirements for the associated transportation and storage infrastructure. Notably, that in the PSA cases, CO is an issue and will need to be significantly reduced in order to meet any of the specifications. Even the CO_2 captured by the amine

Table 5: Comparison of CO_2 specifications for CO_2 transport and storage [16][17][18].

	Limiting concentration criterion		
	Northern Lights[†]	**National Grid***	**TAQA**
CO_2	-	≥ 91 vol% (gaseous phase) ≥ 96 vol% (dense phase)	≥ 95% [‡]
H_2O	≤ 30 ppm$_v$	≤ 50 ppm$_v$	≤ 40 ppm$_v$
O_2	≤ 10 ppm$_v$	≤ 10 ppm$_v$	≤ 40 ppm$_v$
NO_x ($NO+NO_2$)	≤ 10 ppm$_v$	≤ 100 ppm$_v$	≤ 5 ppm$_v$ (≤ 2.5 ppm$_v$ + ≤ 2.5 ppm$_v$)
SO_x	≤ 10 ppm$_v$	≤ 100 ppm$_v$	≤ 50 ppm$_v$
H_2S	≤ 10 ppm$_v$	≤ 20 or 80 ppm$_v$ [§]	≤ 5 ppm$_v$
COS	-	¶	≤ 0.1 ppm$_v$
$(CH_3)_2S$	-	-	≤ 1.1 ppm$_v$
H_2	≤ 50 ppm$_v$	≤ 2 vol%	≤ 0.75 vol%
N_2	-	Depends on saturation P [ǀ]	≤ 2 mol%
Ar	-	Depends on saturation P [ǀ]	≤ 1 mol%
CH_4	-	Depends on saturation P [ǀ]	≤ 1 mol%
CO	≤ 100 ppm$_v$	≤ 2000 ppm$_v$	≤ 750 ppm$_v$
Amine	≤ 100 ppm$_v$	¶	-
NH_3	≤ 10 ppm$_v$	¶	-
HCN	-	¶	≤ 20 ppm$_v$
Formaldehyde	≤ 20 ppm$_v$	-	-
Acetaldehyde	≤ 20 ppm$_v$	-	-
Mercury, Hg	≤ 0.03 ppm$_v$	¶	-
Cadmium, Cd Thallium, Tl	≤ 0.03 ppm$_v$ (sum)	-	-
C2+ (hydrocarbons)	-	-	≤ 1200 ppm$_v$
Aromatics (incl. BTEX)	-	-	≤ 0.1 ppm$_v$
C_2H_4	-	-	≤ 1 ppm$_v$
Total VOC	-	-	≤ 750 ppm$_v$

* Entry may be permitted for compounds other than those listed (Hg + derived compounds, Se, MEA, Selexol, NH_3, HCl, HF, HCN, COS etc.), conditional on them not exceeding detection limits and to be determined on a case by cases basis.

[†] Non-condensable gases are defined in the Northern Lights specification as components that, when pure, will be in gaseous form at 15barg and -26°C, where their content will be limited by the actual solubility in liquid CO_2 in the interim storage tanks at the capture plants.

[‡] The sum of non-condensable species H_2, N_2, Ar, CH_4, CO and N_2 should not exceed 4 vol%.

[§] Limits of 80 and 20 ppm$_v$ apply to gaseous (below 80 barg) and dense (below 156 barg) phases, respectively.

[ǀ] The allowable concentration of non-condensable components is subject to confirmation that the mixture saturation pressure does not exceed 80 barg.

¶ Must not exceed levels above measurable limits and need to be discussed and agreed with National Grid.

system which has the lowest content of CO estimated at 200 ppm$_v$ will not meet the 100 ppm$_v$ threshold for the Northern Lights specification. Other potentially problematic impurities include reduced sulfur compounds, H_2S and COS. Reductions in the content of H_2S in CO_2 for all PSA and amine capture systems appears to be needed while a drastic reduction in COS would be required to meet the TAQA specification. Issues related to SO_x would appear to be less of a concern where all three estimated capture qualities would already meet the required threshold for all CO_2 specifications. Similarly, the nitrogen containing impurities, HCN and NH_3 appear not to need specific targeting by additional separation. To meet the strict limits on water concentration, it is clear that some form of dehydration will be needed to reduce the amounts from saturated levels from the capture systems, although this should not be of great concern due to available technologies being mature and inexpensive. Other potential impurities of concern include H_2 in the case of meeting the Northern Lights specification and O_2 where air ingress may take place in iron and steel plant or CO_2 capture systems. O_2

may also become a problematic impurity in species for other types of technologies that could be employed for CO_2 capture on iron and steel plants such as those that use oxy-combustion based approaches. In the following section, we discuss approaches that can be taken to reduce the impurities of concern in the captured CO_2 from BFG streams.
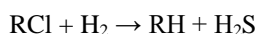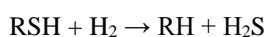
5. CO₂ purification approaches

In this section, approaches to CO_2 purification suitable for CO_2 capture from BFG are discussed with emphasis on targeting the critical contaminants, reduced sulfur species and CO. Multicomponent removal solutions are also outlined.

5.1 Approaches to H₂S and COS reduction

Sulfur components can be removed either by wet scrubbing or by dry adsorption processes. In wet processes, the sulfur components can be removed by physical (e.g. Rectisol) or chemical adsorption (e.g. MEA) or by a combination of both. An example of a dry

process is the adsorption of H_2S on ZnO [19]. Technologies for sulfur reduction should be selected on the basis of inlet and target concentration, while scale is another important factor. Wet processes are characterised by high investment costs and are therefore mainly used at large scale. Dry processes are used mainly for low inlet concentrations and therefore may be suitable for targeting the levels of sulfur in BFG. The ZnO adsorbent process is widely used for H_2S removal (at levels normally <50 ppm) from natural gas or syngas at temperatures of 200−450°C. In a conventional catalytic adsorbent purification system, illustrated in Figure 2, ZnO is used in conjunction with hydrogenation catalysts based on cobalt, molybdenum and nickel. This system involves the hydrogenation of sulfur compounds such as mercaptans to H_2S, and halides such as chlorides to HCl. These compounds are then reacted with the ZnO absorbent where H_2S is converted to zinc sulfide, and HCl forms a stable chloride. Additionally, ZnO removes COS by hydrolysis to form H_2S which is then adsorbed to form zinc sulfide [20]. The general, reactions are summarised as follows:

Hydrogenation reactions:

$$RSH + H_2 \rightarrow RH + H_2S$$

$$RCl + H_2 \rightarrow RH + H_2S$$

Reactions with ZnO:

$$ZnO + H_2S \rightleftharpoons ZnS + H_2O$$
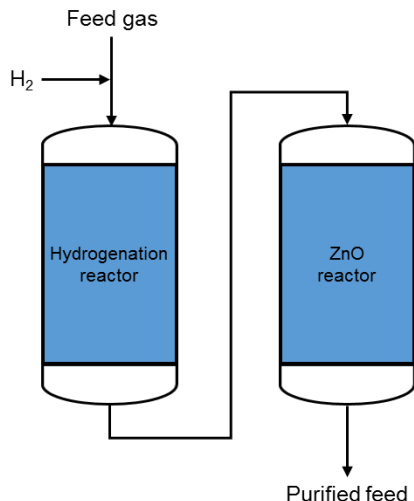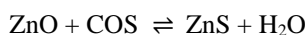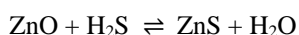
$$ZnO + COS \rightleftharpoons ZnS + H_2O$$

Figure 2: Conventional ZnO purification system [20].

Sulfur removal below 50 ppb_v is attainable with ZnO. However, a hydrogenation reactor may not be required in the case of processing BFG if the presence of halogens and sulfur compounds other than H_2S and COS is not a concern for the downstream impacts. A quantity of 100 kg ZnO is required to remove 39 kg S while the cost of a ZnO sorbent is ~2 $/kg.

5.2 Approaches to CO reduction

Different approaches can be taken for reducing the CO content in captured CO_2 streams that may once again depend on the quantities involved, the inlet and target concentrations. In the case of low purity CO_2 from the

PSA based capture case with 83% purity CO_2, a cryogenic based system is an option to remove CO simultaneously with other non-condensable components. In such a system, CO_2 is liquefied to separate it from the non-condensable gases. The ULCOS program [21] explored the use of PSA and vacuum PSA (vPSA) systems with a subsequent cryogenic separation for achieving high purity CO_2. Cryogenic flash separation is commonly used to treat CO_2 streams with above 80 mol% purity. Higher grades of CO_2 can be produced using cryogenic distillation which have a history of development for oxyfuel combustion power systems, and operate at elevated pressures ~30 bar and low temperatures between -10 °C and -60 °C. The conditions in this process make it energy intensive with an energy requirements for the CO_2 Compression and Purification system (CPU) ranging from of 412 to 700 kJ/kgCO₂. Typical recovery efficiencies are in the range of 86.6 to 90.1% with CO_2 purities as high as 99.99 vol% achievable [22].

Other approaches to CO reduction can involve conversion by reaction to other compounds which are more easily separable or have higher thresholds in the CO_2 specifications. For example, the water gas shift process could be used to convert CO to CO_2 and H_2 but would necessitate both high and low temperature conversion units for deep CO reduction. Employing this process could also lead to improved overall CO_2 capture rates above 80%. Alternatively, CO could be reacted with H_2 to produce CH_4 or with O_2 to produce CO_2. Oxidation as an approach to CO reduction is covered below in the context of multi-component removal approaches.

5.3 Approaches to multicomponent reduction

Catalytic oxidation has been used as an approach to remove ppm levels of impurities from raw CO_2 streams to produce high purity CO_2 product for different applications including for the food industry. Praxair patented a technology for the removal sulfur compounds and hydrocarbons from CO_2, which is also capable of CO reduction [23]. This technology uses a sulfur tolerant catalytic oxidation system whereby contaminants are oxidised to CO_2, water and SO_2 which are then removed by adsorption and/or absorption techniques. While hydrocarbons are converted to CO_2 by the catalytic oxidation process, sulfur compounds (e.g. H_2S, CS_2, COS and mercaptans) present in the CO_2 stream react with O_2, forming their respective combustion products according to the following reactions:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$CS_2 + 3O_2 \rightarrow 2SO_2 + CO_2$$

$$2COS + 3O_2 \rightarrow 2SO_2 + 2CO_2$$
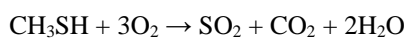
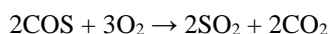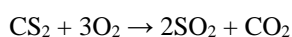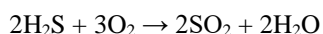$$CH_3SH + 3O_2 \rightarrow SO_2 + CO_2 + 2H_2O$$

Figure 3 presents a simplified process block flow diagram for the purification system by catalytic oxidation. Crude CO_2 first passes through a compression step and liquid water is removed by a separator. In this system, O_2 is injected either as air or PSA produced O_2 to maintain an excess O_2 concentration of approximately 1000 ppm in the gas stream leaving the catalytic

oxidation reactor. The temperature of the gas entering the catalytic reactor is increased to approximately 315 to 480 °C and then passed over a sulfur tolerant metal catalyst (platinum and palladium catalysts are preferred) where the impurities react with the O_2 to form oxidised products. The temperature of the catalytic bed is typically kept below about 425 °C to minimise the oxidation of CH_4 since this contaminant can readily be removed in a subsequent CO_2 liquefaction/stripper stage. The catalytic oxidiser is operated at preferred pressure of about 17 to 22 bar. After the hydrocarbon contaminants and the sulfur compounds are converted to their respective oxides, upon exiting the catalytic oxidiser, the gas stream is cooled by means of a cooler/condenser and condensed

water is removed using a water separator. The sulfur oxides are next subsequently removed from the CO_2 stream by absorption, for high concentrations of sulfur components (e.g. ~100-5000 ppm), or by adsorption, for low concentration of sulfur components (e.g. ~1-100 ppm). The gas stream (which now is free of sulfur, hydrocarbon compounds and water) enters the CO_2 liquefier, where the non-condensables (e.g. O_2, N_2 and CH_4) are separated by distillation and vented from the liquid CO_2 stream. The process is claimed to produce CO_2 at a quality of 99.9 vol% CO_2 with $N_2 < 60$ ppm$_v$, $O_2 < 30$ ppm$_v$, sulfur species < 1 ppm$_v$, total hydrocarbons <20 ppm$_v$ and water < 20 ppm$_v$ and at a temperature of -18 °C and pressure of 10 bar.
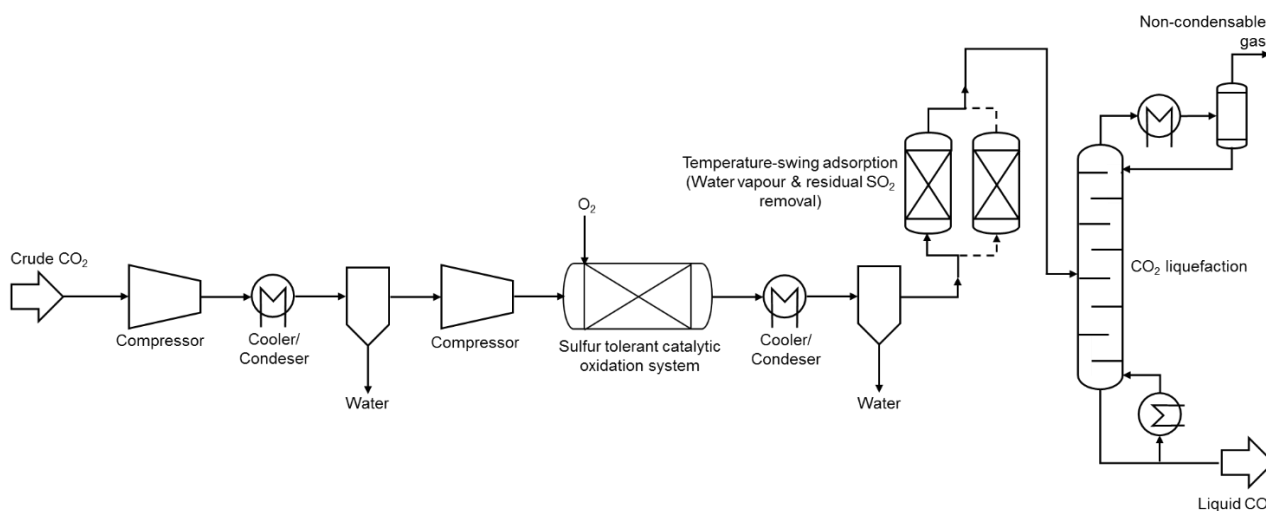

Figure 2: Block flow diagram of CO_2 purification process by catalytic oxidation (based on [23]).

Other embodiments of the above process have been proposed where the excess O_2 is chemisorbed by a bed of transition metal adsorbent (i.e., Cu or Ni) in place of a distillation system, or where the excess oxygen leaving the catalytic oxidation system is controlled to less than 30 ppm by using a "*tight control*" option [23].

At the time of writing, no detailed techno-economic studies of CO_2 purification by catalytic oxidation for removal of CO and sulfur components are available in the literature.

5.4 Water removal technologies

Dehydration of CO_2 streams can be carried out using several technologies, including compression and cooling, adsorption using solid desiccants, absorption using liquid desiccants, absorption with a deliquescent solid, and cooling below the initial dew point [24].

Guidelines for the selection of dehydration technology for carbon capture systems have been put forward by Kemper et al. [25] which allocates a range of technologies, such as TEG (triethylene glycol) and molecular sieve systems, applicable to certain ranges of wet gas water content and a target dry gas concentrations. These authors also noted that the presence of impurities, i.e. NO_x, SO_x and H_2S, leads to a 7% higher capital expenditure (CAPEX) but no difference in operational expenditure (OPEX) for molecular sieve systems. For the

iron and steel industry, the derived CO_2 product streams presented in table 4 and the target concentrations of European CO_2 specifications listed in table 5, molecular sieve and silica gel systems are the most likely technologies for implementation.

6. Conclusion

This paper has reviewed the range and level of impurity components in steelworks off-gases and provided estimates of their carry over into CO_2 product streams when primary capture steps of PSA (low and high purity scenarios) and amine scrubbing are applied to BFG. While useful insight can be gleaned from these estimates, they require further assessment by experimental investigation and detailed process simulation studies. European CO_2 transportation and storage specifications have been reviewed and compared, with the implications for the impurity content of CO_2 streams captured from BFG. In many cases, additional gas clean-up measures will likely be needed if the CO_2 specifications for impurity limits that are currently imposed by CO_2 transportation and storage providers are to be met. Particular CO_2 impurities of concern that require reduction for the presented applications of CCS in the iron and steel industry are CO and the reduced sulfur species H_2S and COS. Dehydration systems will also be needed for CO_2 product processing. Options for removing sulfur components suitable for the levels

present in BFG focus on adsorption based systems, while CO reduction techniques for impure CO_2 involve cryogenic separations. Multicomponent removal methods for CO and sulfur species involve catalytic oxidation followed by adsorption/absorption and cryogenic separation.

It should be noted that reasonable limits on impurities in CO_2 must be set on the basis of safety, design, operation, integrity and hydraulic efficiency of the associated transportation and storage infrastructure and these requirements have to be considered as a whole. Thresholds which are excessively stringent for impurities in CO_2 transportation and storage specifications will cause a financial burden on CO_2 emitters due to the associated costs of removal, therefore posing a potential barrier to CCS deployment. Conversely, the emission of high levels of impurities in CO_2 product streams into infrastructure could move the financial burden onto transportation and storage providers. Techno-economic analysis techniques should be employed to consider site-specific design and operation of the CCS chain during normal and abnormal operation in order to achieve an optimised balance between the cost of purification and the impacts of impurities on CO_2 transportation and storage infrastructure.

Acknowledgements

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