Session 5C Panel discussion 3:

CO_2 Impurities and Implications for Multiple Source Networks and Hubs

Lead Panellist: Haroun Mahgerefteh, University College London.

Panellists:

Richard Porter – University College London
Opportunities and challenges of achieving European CO_2 transport specifications
Simon Roussanaly – Sintef
Impact of impurities in tanked-based transport of CO_2
Heike Rütters – BGR
Impacts of impurities on the storage infrastructure/site
Filip Neele – TNO
Techno-economic trade-offs for CO_2 impurities in CCUS chain integration

C⁴U

Challenges and opportunities of achieving European CO_2 transportation and storage specifications

Richard Porter[1]

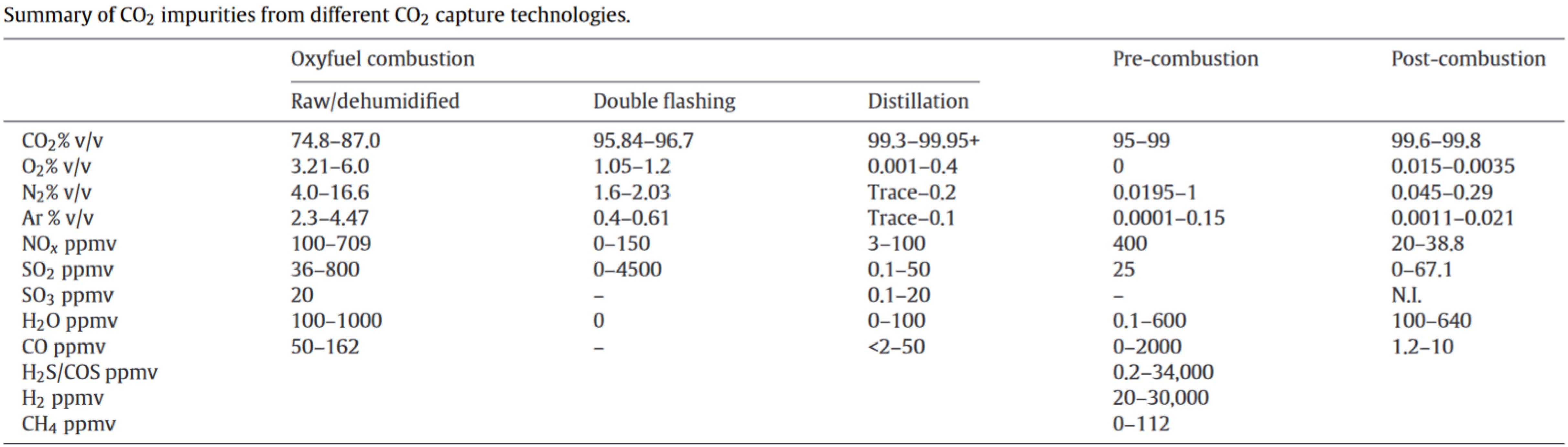
Acknowledgements: Julian Barnett[2], Paul Cobden[3], Eric De Coninck[4], Haroun Mahgerefteh[1], Giampaolo Manzolini[5], Sergey Martynov[1], Fabio Ruggeri[6], Vincenzo Spallina[7]

1 UCL
2 nationalgrid
3 SWERIM
4 ArcelorMittal
5 wood.
6 POLITECNICO MILANO 1863
7 MANCHESTER 1824 The University of Manchester

25 October 2022

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

Range and level of impurities in CO_2 product streams (coal power CCS)



Summary of CO_2 impurities from different CO_2 capture technologies.

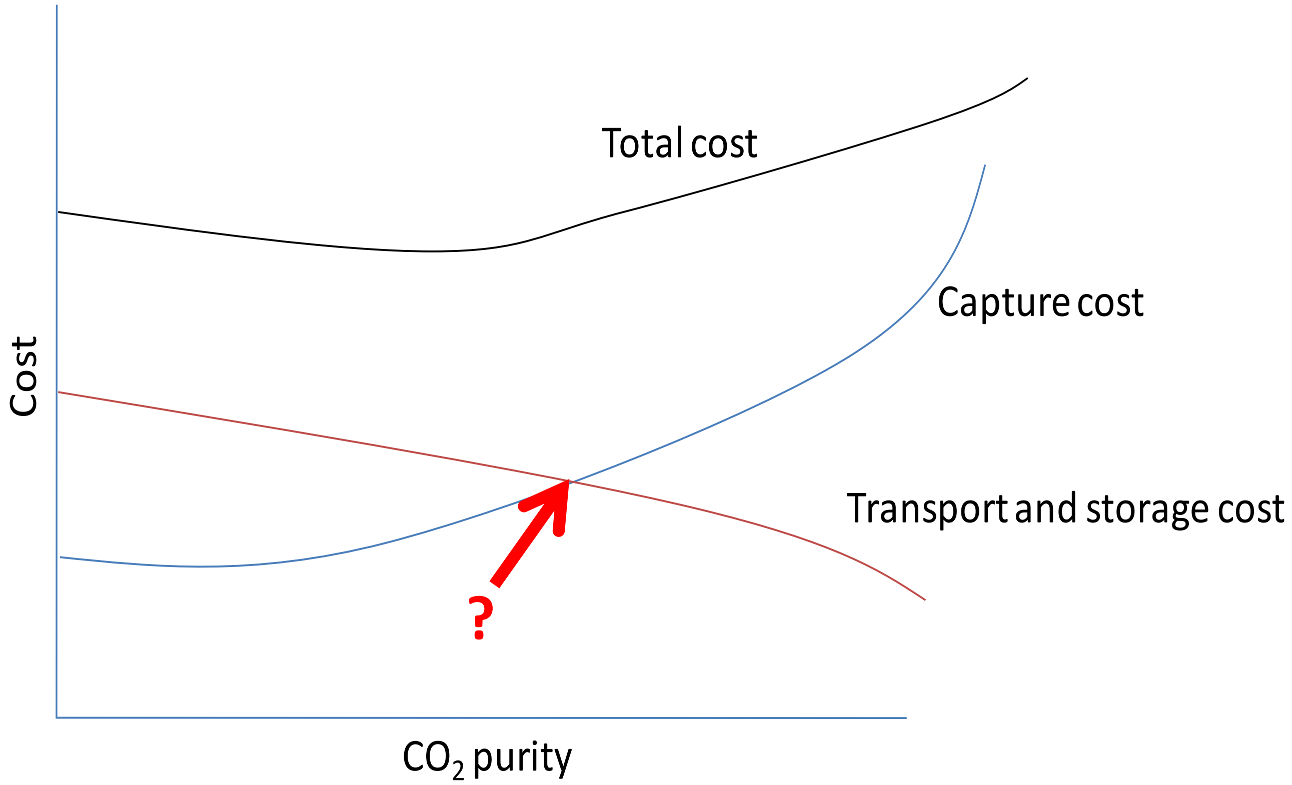
	Oxyfuel combustion			Pre-combustion	Post-combustion
	Raw/dehumidified	Double flashing	Distillation		
CO_2% v/v	74.8–87.0	95.84–96.7	99.3–99.95+	95–99	99.6–99.8
O_2% v/v	3.21–6.0	1.05–1.2	0.001–0.4	0	0.015–0.0035
N_2% v/v	4.0–16.6	1.6–2.03	Trace–0.2	0.0195–1	0.045–0.29
Ar % v/v	2.3–4.47	0.4–0.61	Trace–0.1	0.0001–0.15	0.0011–0.021
NO_x ppmv	100–709	0–150	3–100	400	20–38.8
SO_2 ppmv	36–800	0–4500	0.1–50	25	0–67.1
SO_3 ppmv	20	–	0.1–20	–	N.I.
H_2O ppmv	100–1000	0	0–100	0.1–600	100–640
CO ppmv	50–162	–	<2–50	0–2000	1.2–10
H_2S/COS ppmv				0.2–34,000	
H_2 ppmv				20–30,000	
CH_4 ppmv				0–112	

- ☐ ppb – ppm levels of heavy metals (Hg/$HgCl_2$, Pb, Se, As, etc.) and (poly)aromatics
- ☐ Natural gas combustion likely to produce lower levels of sulfur oxides and nitrous oxides, but higher oxygen compared to coal combustion

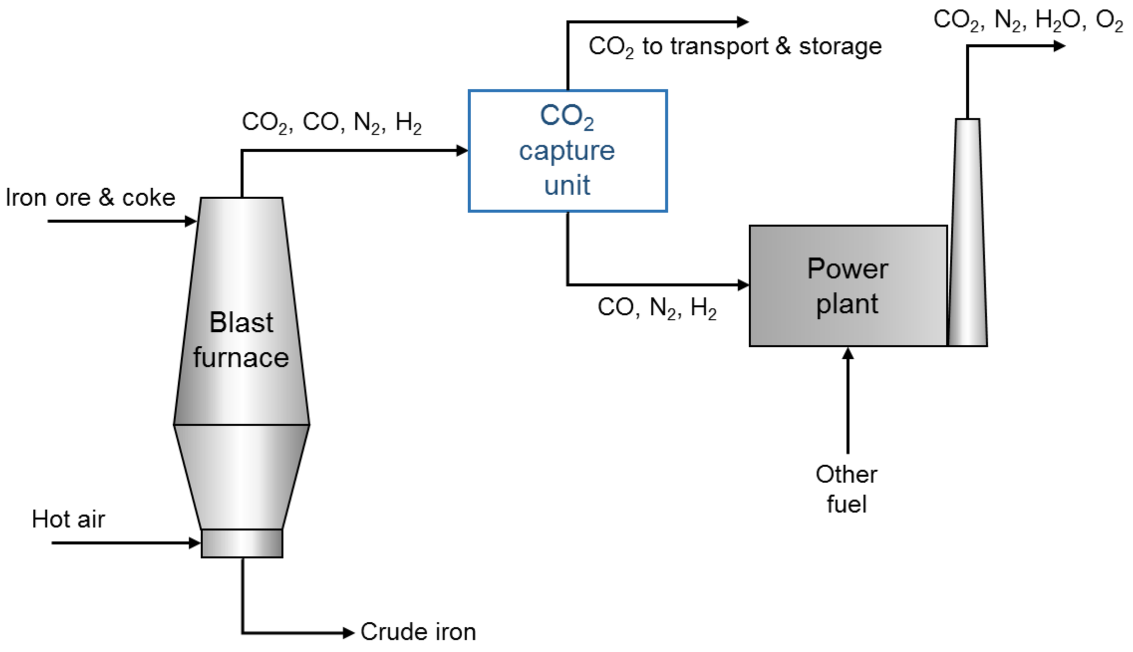
R.T.J. Porter, M. Fairweather, M. Pourkashanian and R. M. Woolley. Int. J. Greenhouse Gas Control, 2015, 36, 161–174.

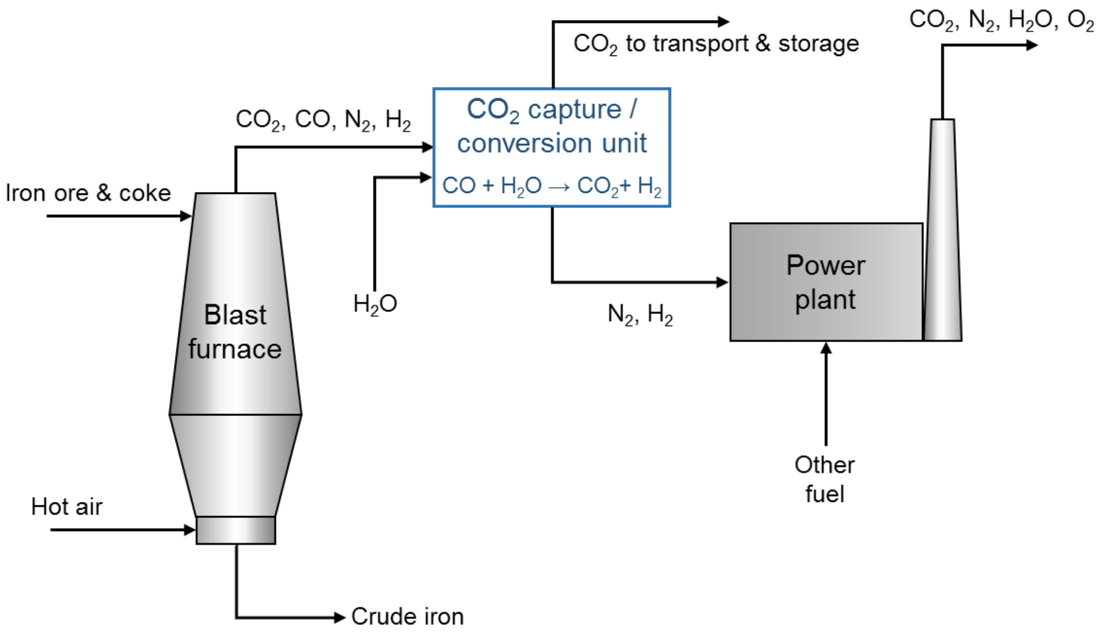
The m$ Question?

What is the optimum range and concentration of impurities that can be tolerated in the CO_2 stream to enable its safe transportation and storage at minimum cost?



Concepts for CO_2 capture / conversion from Blast Furnace Gas





Benchmark type processes

e.g., PSA (Pressure Swing Adsorption)

MEA (Monoethanolamine)

Advanced capture technologies

e.g., SEWGS (Sorption Enhanced Water Gas Shift)

CASOH (Calcium Assisted Steel-mill Off-gas Hydrogen production)

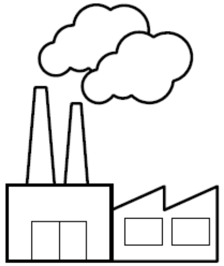
Potential impurities in steelworks off-gases

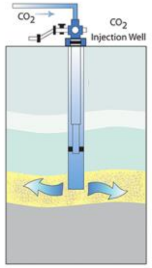
Compound class	Compound
Hydrocarbons	CH_4, C_2H_4, C_2H_6, cyclopentadiene, C_3H_8, C_3H_6, C_4H_{10}, acetylene, pentene, heavy hydrocarbons
Aromatics	Phenol, benzene, toluene, xylene
PAH	Naphthalene, phenanthrene, benzopyrene, flouranthene
S-compounds	SO_x (SO_2), H_2S, COS, CS_2, thiophene, mercaptan
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

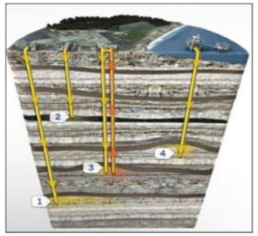
PAH: Poly aromatic hydrocarbon;
PCCD/F: Polychlorinated benzo(p)dioxin and furan.

(Carbon2Chem Project) - J. Schittkowski *et al. Methanol Synthesis from Steel Mill Exhaust Gases: Challenges for the Industrial Cu/ZnO/Al_2O_3 Catalyst.* Chem. Ing. Tech., 90 (2018), pp. 1419-1429.

CCUS chain impurities issues







CCUS chain element	**Capture, Purification, Utilisation compression**	**CO_2 pipeline**	**CO_2 injection well**	**Geological storage formation**
CO_2 impurities issues	Corrosion; Materials impact; Catalyst deactivation; Cost of removal; Cost of compression; Environmental health.	Corrosion; Phase behaviour; Hydrates formation; Fracture propagation; Environmental health; Odour.	Well component corrosion – pitting / cracking; Injection power; Environmental health.	**Physical effects:** Storage capacity; Plume migration. **Chemical effects:** Mineral dissolution; Mineral precipitation; Oxidation.

CO_2 composition (H_2O, O_2, NOx, SOx, H_2S, CO…)

CO_2 transport to geological storage site

Two main options for large-scale CO_2 transportation:

Onshore and/or offshore CO_2 pipeline

Gas-phase: up to 35 bar, 5 to 40 °C

Dense-phase: 85 to 150 bar, 12 to 44 °C

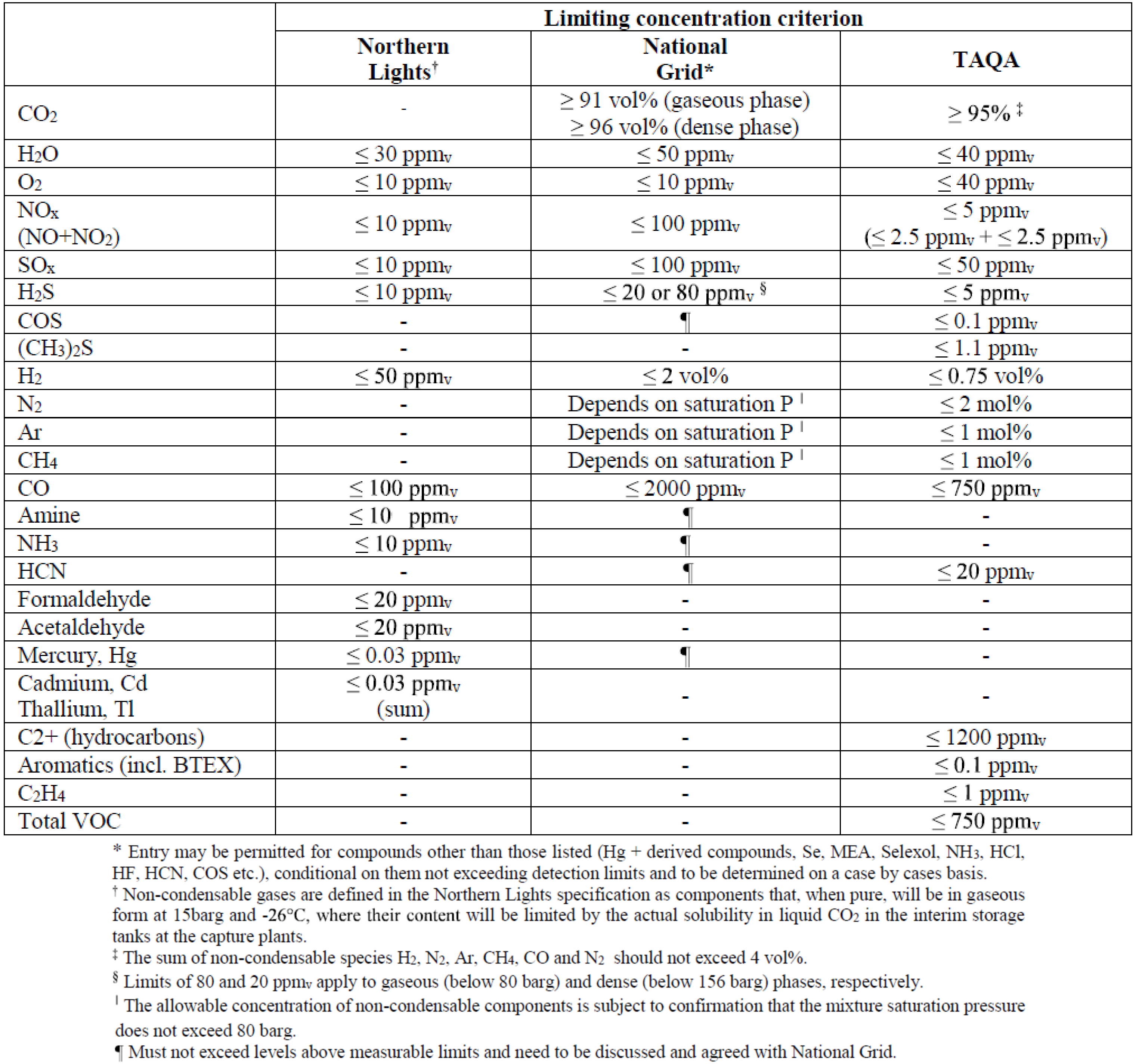
CO_2 shipping (offshore)

Liquid-phase: 6 to 30 bar, -50 to -20 °C

CO_2 specifications comparison

Challenge for other CCS applications

Purity specification challenge, specifically for the iron & steel industry



	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	≤ 10 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.

References

Norwegian CCS Demonstration Project Norcem FEED: https://ccsnorway.com/wp-content/uploads/sites/6/2020/07/NC03-NOCE-A-RA-0009-Redacted-FEED-Study-DG3-Report-Rev01-1.pdf

National Grid carbon specification for carbon dioxide quality requirements for pipeline transportation. NGC/SP/PIP/25, National Grid, 2019.

TAQA - PORTHOS Basis of completion design report: https://www.rvo.nl/sites/default/files/2020/09/Bijlagen%20Ondergrond.pdf (pp. 519).

Estimated impurities in CO_2 capture from Blast Furnace Gas (BFG)

Main impurities in CO_2 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 ppm_v
H_2 -	0.96%	266 ppm_v	214 ppm_v
COS ppm_v	163	214	131
H_2S ppm_v	50.8	66.9	41
SO_2 ppm_v	1.1	1.4	0.9
HCN ppm_v	0.02	0.001	0.45
NH_3 ppm_v	0.05	0.0007	0.88
HCl ppm_v	0.04	0.001	0.71
Amine ppm_v	-	-	<1

Assumed BFG composition:

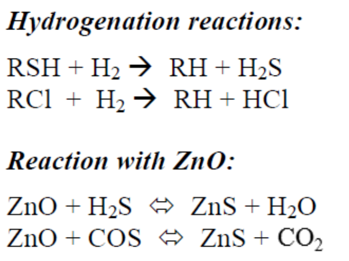
BFG component		
AR	0.61	mol%
H_2	4.26	mol%
N_2	47.09	mol%
CO_2	24.37	mol%
CO	23.45	mol%
CH_4	238.00	ppm_v
H_2S	10.00	ppm_v
COS	32.00	ppm_v
SO_2	0.21	ppm_v
HCl	0.17	ppm_v
HCN	0.11	ppm_v
NH_3	0.21	ppm_v

References for BFG composition

[1] R. Remus et al. Best Available Techniques (BAT) Reference Document for Iron and Steel Production: Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), JRC Reference Report, EC, JRC, Institute for Prospective Technological Studies, Seville 2013.
[2] Lanzerstorfer, C.; Preitschopf, W.; Neuhold, R.; Feilmayr, C. ISIJ Int. 2019,59(3), 590−595.

Potential CO_2 purifications for BFG derived CO_2 product streams

ZnO is a widely used adsorbent for H_2S and COS removal (at levels <50ppm) from NG or syngas at 200−450°C.



Hydrogenation reactions:

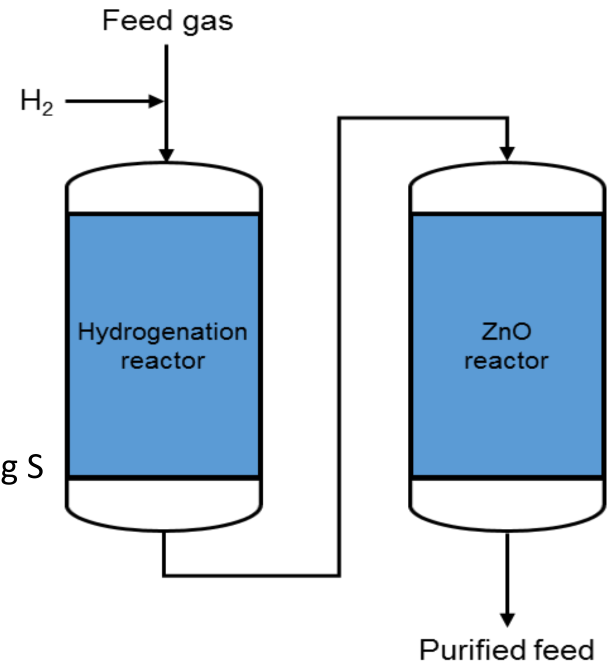
$RSH + H_2 \rightarrow RH + H_2S$

$RCl + H_2 \rightarrow RH + HCl$

Reaction with ZnO:

$ZnO + H_2S \Leftrightarrow ZnS + H_2O$

$ZnO + COS \Leftrightarrow ZnS + CO_2$



100 kg ZnO removes 39 kg S
ZnO sorbent ~ 2 $/kg

+ Cryogenic separation of non-condensables (H_2, N_2, Ar, CH_4, CO, O_2)

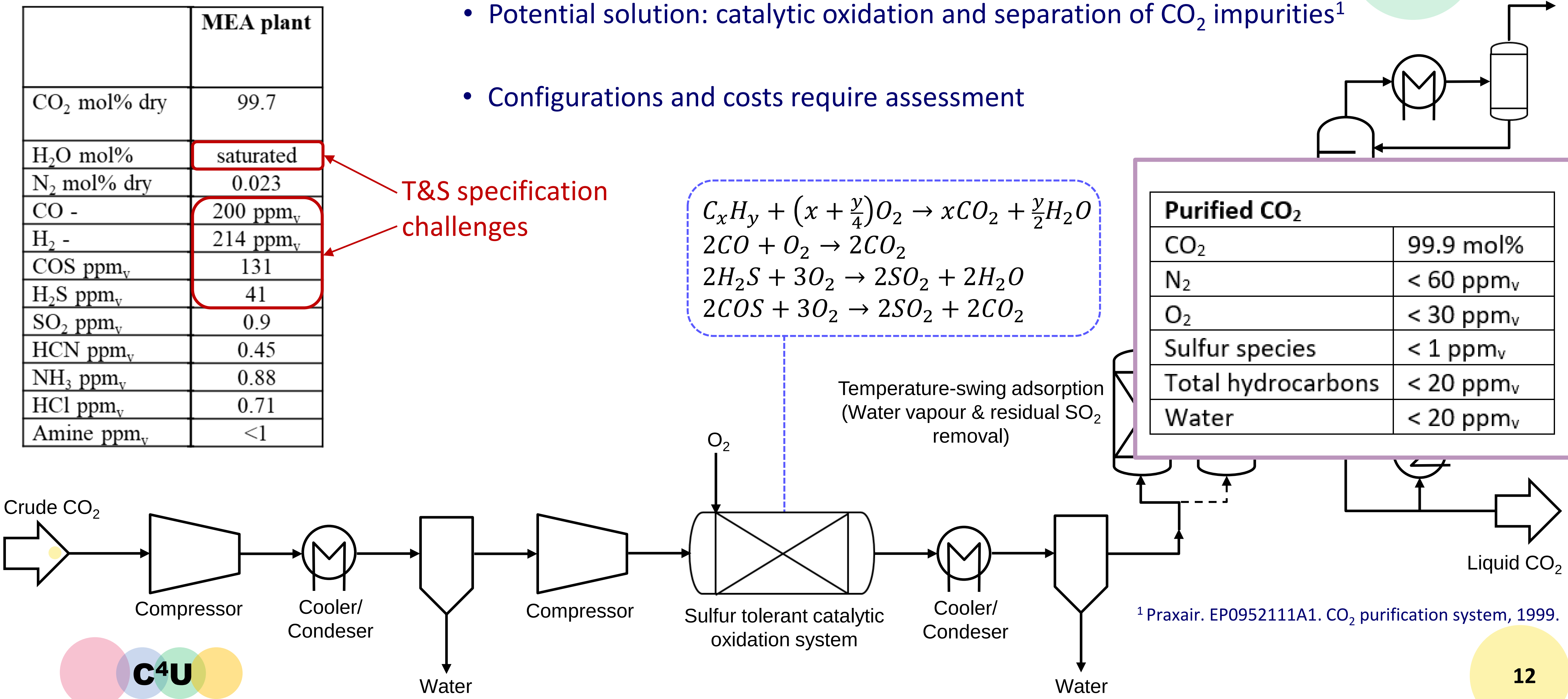
Purification of Blast Furnace Gas derived crude CO_2 streams

	MEA plant
CO_2 mol% dry	99.7
H_2O mol%	saturated
N_2 mol% dry	0.023
CO -	200 ppm_v
H_2 -	214 ppm_v
COS ppm_v	131
H_2S ppm_v	41
SO_2 ppm_v	0.9
HCN ppm_v	0.45
NH_3 ppm_v	0.88
HCl ppm_v	0.71
Amine ppm_v	<1

T&S specification challenges

- Potential solution: catalytic oxidation and separation of CO_2 impurities[1]
- Configurations and costs require assessment

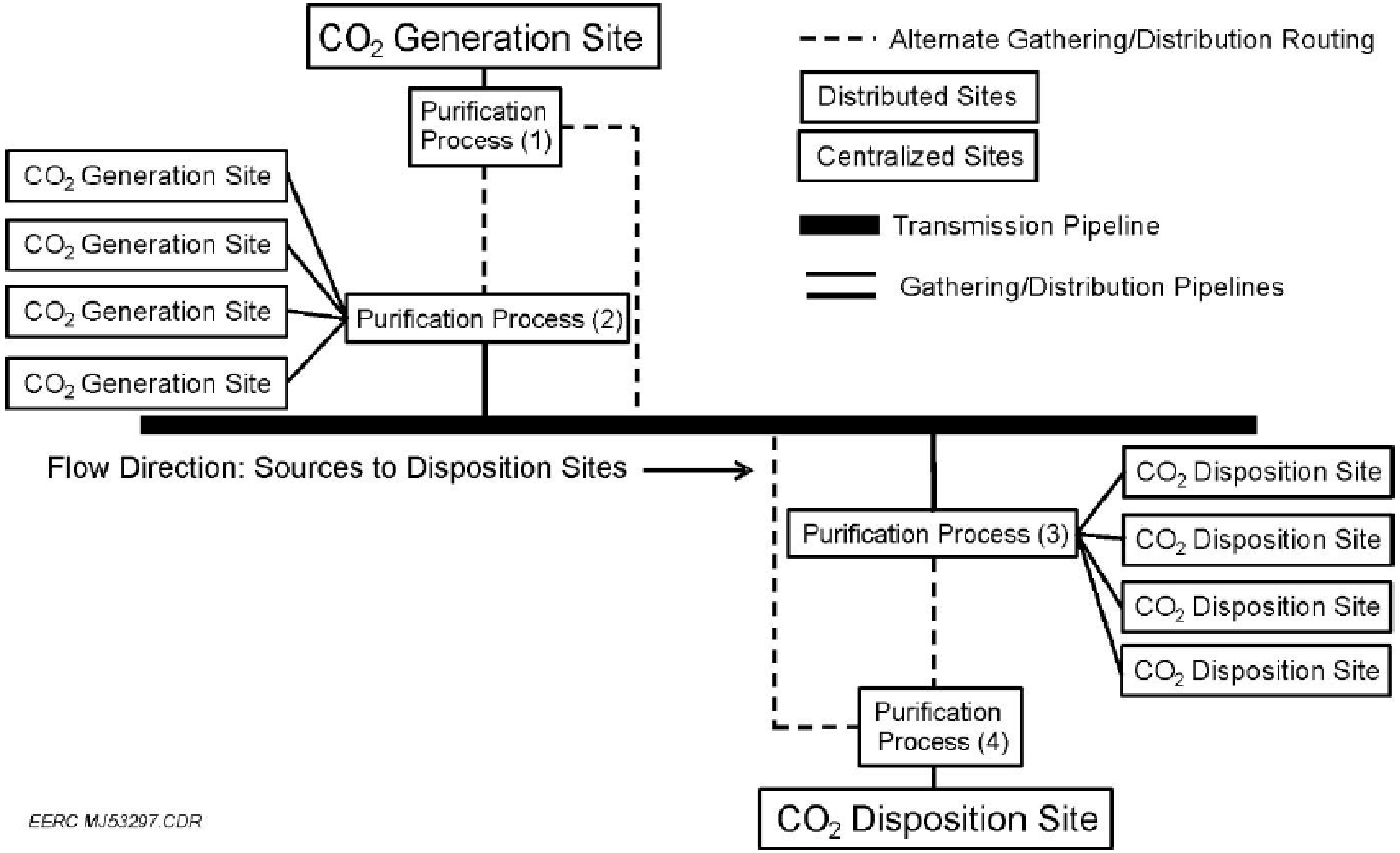
$$C_xH_y + \left(x + \tfrac{y}{4}\right)O_2 \rightarrow xCO_2 + \tfrac{y}{2}H_2O$$
$$2CO + O_2 \rightarrow 2CO_2$$
$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$
$$2COS + 3O_2 \rightarrow 2SO_2 + 2CO_2$$



Purified CO_2	
CO_2	99.9 mol%
N_2	< 60 ppm_v
O_2	< 30 ppm_v
Sulfur species	< 1 ppm_v
Total hydrocarbons	< 20 ppm_v
Water	< 20 ppm_v

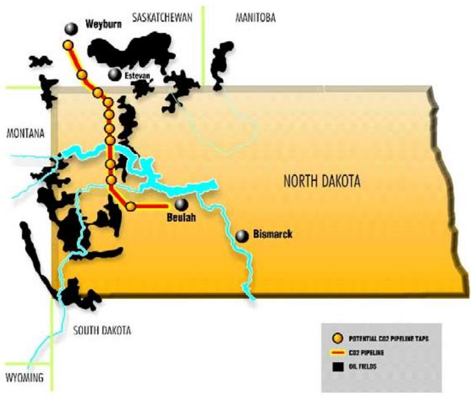
[1] Praxair. EP0952111A1. CO_2 purification system, 1999.

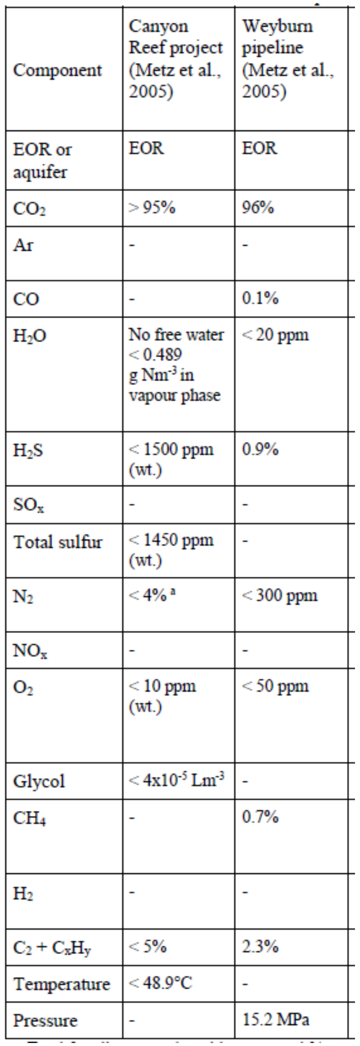
Centralised vs decentralised CO_2 purification



Andrea Dunn. Opportunities and challenges associated with CO_2 compression and transport during CCS activities. Plains CO_2 Reduction Partnership Phase III.

Concluding remarks





Component	Canyon Reef project (Metz et al., 2005)	Weyburn pipeline (Metz et al., 2005)
EOR or aquifer	EOR	EOR
CO_2	> 95%	96%
Ar	-	-
CO	-	0.1%
H_2O	No free water < 0.489 g Nm^{-3} in vapour phase	< 20 ppm
H_2S	< 1500 ppm (wt.)	0.9%
SO_x	-	-
Total sulfur	< 1450 ppm (wt.)	-
N_2	< 4% [a]	< 300 ppm
NO_x	-	-
O_2	< 10 ppm (wt.)	< 50 ppm
Glycol	< $4x10^{-5}$ Lm^{-3}	-
CH_4	-	0.7%
H_2	-	-
$C_2 + C_xH_y$	< 5%	2.3%
Temperature	< 48.9°C	-
Pressure	-	15.2 MPa

There are significant differences in the CO_2 storage specification depending on the project.

Pipeline transport and storage of CO_2 with relatively high concentration of some impurities are technically feasible (e.g. CO, H_2S), as demonstrated by the North American EOR experience; however, this may be undesired in the European context

Challenges

1. Need to perform whole chain integration techno-economic analysis and optimisation (i.e. cost of purification vs cost of using more corrosion resistant materials)
2. Need to reduce uncertainties on the impacts of impurities in CCS chain elements
3. Need to ‘strategically’ reach a closer agreement for the CO_2 specifications levels as this could well become a potential show stopper to CCS development