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Performance data and solvent degradation and management for concentrated MEA and an advanced amine blend

CCUS Innovation 2.0
Key Knowledge Deliverable 3.2 & 3.3

November 2023

Key Knowledge Deliverable Cover Sheet

This Key Knowledge Deliverable (KKD) has been produced by the Translational Energy Research Centre at the University of Sheffield as part of the Department for Energy Security and Net Zero £1bn Net Zero Innovation Portfolio (NZIP) - CCUS Innovation 2.0 programme. The document is reflective of the status of the project at the time of writing. The material presented could be subject to change as the project matures. These documents should not be considered a full representation of the final project.

UK BECCS-MCFC: Next Generation CCUS Technology for Net-Zero 2050

Baseline Test Work: Solvent Performance and Degradation - Reporting performance data for concentrated MEA and advanced amine blend, and concerning degradation and mitigation, technoeconomic data.

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Contents

Performance data and solvent degradation and management for concentrated MEA and an advanced amine blend

The purpose of this report is to discuss key performance characteristics, based on analysis of published information, for two potential solvents for use in a BECCS plant with amine post-combustion capture:

a) MEA at 35% w/w concentration

b) CESAR 1 – a mixture of 13 %w/w piperazine (PZ) and 27% w/w AMP

The key performance characteristics are:

i) Biomass plant flue gas cleaning required for NOx, SOx and particulates

ii) Solvent Degradation: solvent reclaiming or cleaning

iii) Solvent Degradation: acid wash for amine and degradation product emissions control

iv) CO2 capture rate and energy requirements

This report covers Deliverable 3.2 ‘Performance data and solvent management for concentrated MEA and advanced amine blend’ and Deliverable 3.3 ‘Solvent degradation’, with the two deliverables incorporated in the one report to allow the critical interactions between these two topics to be presented and discussed.

Glossary

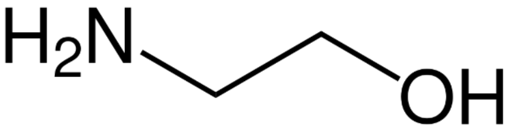
AMP	Aminomethyl Propanol
bara	Bars Absolute (absolute pressure in bars, i.e. units of 10^5 Pa)
barg	Bars gauge, pressure in relation to atmospheric pressure
BAT	Best Available Technology
BD3	Boundary Dam power plant, Unit 3; the first power plant fitted with PCC
BECCS	Biomass Energy with Carbon Capture and Storage
BREF LCP	The BAT Reference Document (BREF) for Large Combustion Plants (BREF LCP, 2017)
CCGT	Combined Cycle Gas Turbine power plant
CCS	Carbon (dioxide) Capture and Storage
CCU	Carbon (dioxide) Capture and Utilisation, not involving permanent storage of the CO_2
CCUS	Carbon (dioxide) Capture, Utilisation and Storage (overwhelmingly EOR at present)
CDR	Carbon Dioxide Removal from the air
CFB	Circulating Fluidised Bed boiler/steam power plant
CHP	Combined Heat and Power plant
CO_2	Carbon dioxide
COPx	The Coefficient Of Performance for (steam) e**x**traction; ratio of heat supplied to a PCC plant by steam extracted from a steam cycle to the reduction in work (electricity) output from that steam cycle
DCC	Direct Contact Cooler; brings the flue gas into contact with water upstream of the absorber, possibly with added caustic to neutralise acid gases
DESNZ	Department for Energy Security & Net Zero, see https://www.gov.uk/government/organisations/department-for-energy-security-and-net-zero
DPA	Dispatchable Power Agreement, see https://www.gov.uk/government/publications/carbon-capture-usage-and-storage-ccus-business-models
EAL	Environmental Assessment Level
EfW	Energy from Waste
ELV	Emission Limit Value
EOP	Electricity Output Penalty
ESP	Electrostatic Precipitator
FCC	Fluid Catalytic Cracker
FGD	Flue Gas Desulphurisation plant
FWH	Feed Water Heater (in a steam boiler)
GT	Gas Turbine

HCl	Hydrogen Chloride (Hydrochloric Acid when dissolved in water)
HHV	Higher Heating Value (also known as gross calorific value)
HF	Hydrogen Fluoride (Hyfluoric Acid when dissolved in water)
HP	High Pressure, the highest pressure cylinder in a steam turbine
HRSG	Heat Recovery Steam Generator (sometimes pronounced “hersig”)
HSS	Heat Stable Salts
IP	Intermediate Pressure, the intermediate pressure cylinder in a steam turbine
IX	Ion exchange reclaimer unit
LC MS QQQ	Liquid Chromatography with triple-Quadrapole Mass Spectrometry
LHV	Lower Heating Value (also known as net calorific value)
LP	Low Pressure, the lowest pressure cylinder in a steam turbine
MEA	Monoethanolamine
MHI	Mitsubishi Heavy Industries
MSG	Minimum Stable Generation
NCCC	National Carbon Capture Center https://www.nationalcarboncapturecenter.com/
NETL	National Energy Technology Laboratory https://www.netl.doe.gov/
NGCC	Natural Gas Combined Cycle
NH_3	Ammonia
NOx	Oxides of Nitrogen
NPC	National Petroleum Council https://www.npc.org/
O_2	Oxygen
OEM	Original Equipment Manufacturer
Pa	Pascal, unit of pressure, $1N/m^2$
PAC	Powdered Activated Carbon
PCC	Post-combustion (CO_2) capture
ppm	parts per million
ppmv, ppbv	parts per million by volume; parts per billion by volume
PTR-TOF-MS	Proton-transfer-reaction time-of-flight mass-spectrometer. Used to measure VOCs. Similarly, QMS = quadrupole-mass-spectrometer
PZ	Piperazine
RAMO	Reliability, Availability, Maintainability, Operability
RFCC	Residual Fluid Catalytic Cracker
RH	Reheat(er) (in a steam boiler)
SCR	Selective Catalytic Reduction (of NOx)
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide (with water, forms sulphuric acid)
SOx	Oxides of Sulphur (unspecified mix of SO_2 and SO_3)
SRD	Specific Reboiler Duty

ST	Steam Turbine
STG	Steam Turbine Generator
T&S	(CO_2) Transport and Storage
TCM	Technology Centre Mongstad https://tcmda.com/
TEA	Techno-Economic Analysis
TERC	Translational Energy Research Centre, University of Sheffield https://terc.ac.uk/
TONO	Total nitrosamines
tpd	tonnes per day
TPY	Tonnes Per Year
TRU	Thermal Reclaimer Unit
VLE	Vapour Liquid Equilibrium
VOC	Volatile Organic Compounds
WESP	Wet ElectroStatic Precipitator
XFHE	The cross-Flow Heat Exchanger, transferring heat from the hot lean solvent leaving the stripper to the cooler rich solvent coming from the absorber

Solvent descriptions and initial comparison

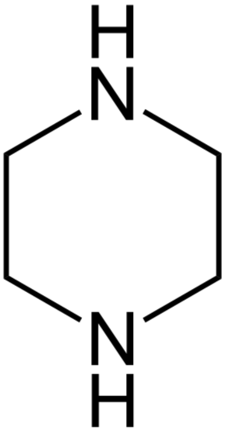
Monoethanolamine



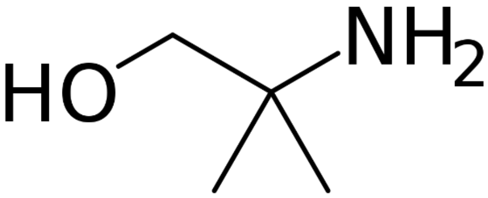
Chemical structure of Monoethanolamine (Wikimedia)

Monoethanolamine is a primary amine with the structure shown above. It is typically used at concentrations of 30-35% w/w in water, occasionally up to 40% w/w. It has seen extensive long-term use for flue gas CO_2 capture, mostly in smaller plants to date.

CESAR1 – PZ and AMP blend



Piperazine structure



Aminomethyl propanol structure

CESAR1[1] is a blend of 26.7 wt% (3.0 M) 2-amino-2-methylpropan-1-ol (AMP) and 12.9 wt% (1.5 M) piperazine (PZ)).

AMP is the sterically hindered form of the primary amine MEA. Piperazine is a cyclic ethylene amine with two secondary amine groups. CESAR1 has been used in a number of research projects but has no commercial deployment examples. It is named after the original project that pioneered its use ‘CESAR: CO_2 Enhanced Separation and Recovery’[2].

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[1] https://gassnova.no/app/uploads/sites/5/2022/04/10-CESAR-1-Solvent.pdf
[2] https://cordis.europa.eu/project/id/213569/reporting

Initial comparison between MEA and CESAR1 components

NETL (2015)[3] gives a summary of solvent properties relevant for commercial use based on the NETL test programme:

> *Primary and secondary amines typically have higher rates of reaction with CO_2 compared to tertiary amines. Among various primary amines, MEA has the highest reaction rate, and blends of MEA and other tertiary or hindered amines are typically used to exploit this feature while maintaining relatively-low reboiler loads. Primary/secondary (mono)amines with a 1:2 stoichiometry have lower CO_2 carrying capacity compared to tertiary amines which bind 1:1 with CO_2. Further, polyamines such as piperazine have a higher carrying capacity because they have two amine groups per molecule. Tertiary amines have higher CO_2 capacities but the reaction kinetics with CO_2 are significantly slower than primary and secondary amines. Because the CO_2 carrying capacity is expressed in wt% CO_2 in the solvent, or the quantity of solvent circulated to capture a unit quantity of CO_2, the molecular weight and density of the solvent also play a role in determining its volumetric or weight-based CO_2 carrying capacity.*
>
> *From a health and environmental safety perspective, MEA is highly biodegradable, and has no direct adverse effects on human health, animals, and vegetation. Other amine solvents such as AMP, MDEA and PZ are toxic and are not easily biodegraded compared with MEA. The reaction of amines with NOx in the flue gas leads to the formation of nitrosamines, which are carcinogenic. The reactivity with NOx varies with the amine structure.*

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[3] NETL (2015) *DOE/NETL Carbon Capture Program—Carbon Dioxide Capture Handbook*, August 2015. https://www.netl.doe.gov/sites/default/files/netl-file/Carbon-Dioxide-Capture-Handbook-2015.pdf

Biomass plant flue gas cleaning required for NOx, SOx and particulates

Expected Best Available Technology pollutant levels for biomass power plants

BREF pollutant emissions from the ‘UK Interpretation Guidance and Permitting Advice on the Best Available Techniques (BAT) Conclusions for Large Combustion Plants (LCPs)’[4] are as follows (original table numbers retained for ease of referencing by readers):

Note approximate conversion factors as follows:

SO_2 mg/Nm^3 to ppmv = x 0.35; NO mg/Nm^3 to ppmv = x 0.75

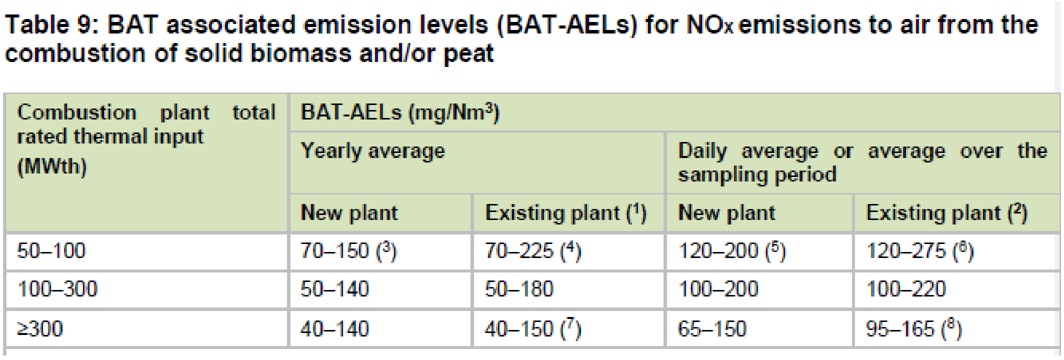

Table 9: BAT associated emission levels (BAT-AELs) for NO_x emissions to air from the combustion of solid biomass and/or peat

Combustion plant total rated thermal input (MWth)	BAT-AELs (mg/Nm³)			
	Yearly average		Daily average or average over the sampling period	
	New plant	Existing plant (1)	New plant	Existing plant (2)
50–100	70–150 (3)	70–225 (4)	120–200 (5)	120–275 (6)
100–300	50–140	50–180	100–200	100–220
≥300	40–140	40–150 (7)	65–150	95–165 (8)

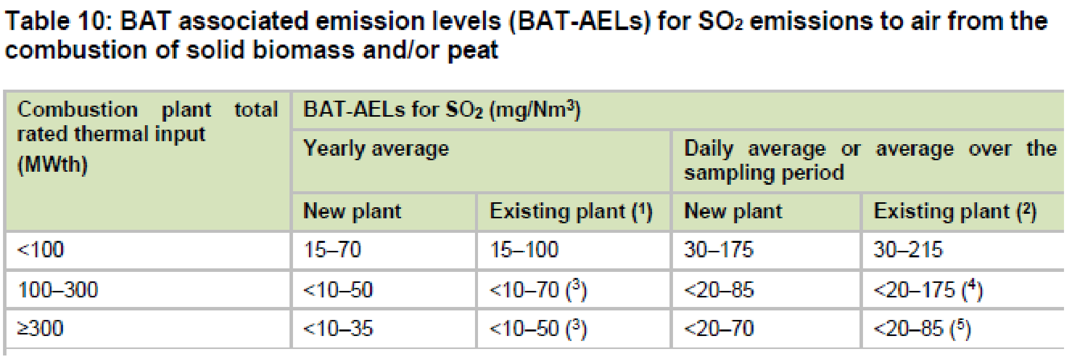

Table 10: BAT associated emission levels (BAT-AELs) for SO_2 emissions to air from the combustion of solid biomass and/or peat

Combustion plant total rated thermal input (MWth)	BAT-AELs for SO_2 (mg/Nm³)			
	Yearly average		Daily average or average over the sampling period	
	New plant	Existing plant (1)	New plant	Existing plant (2)
<100	15–70	15–100	30–175	30–215
100–300	<10–50	<10–70 (3)	<20–85	<20–175 (4)
≥300	<10–35	<10–50 (3)	<20–70	<20–85 (5)

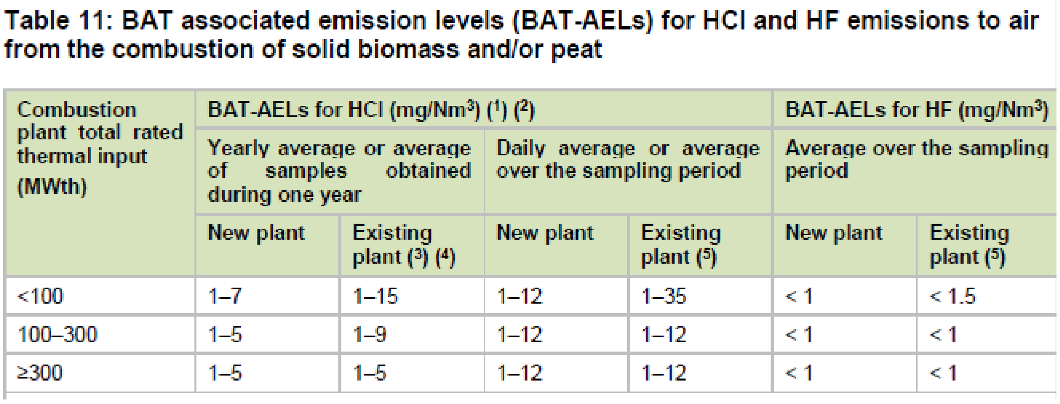

Table 11: BAT associated emission levels (BAT-AELs) for HCl and HF emissions to air from the combustion of solid biomass and/or peat

Combustion plant total rated thermal input (MWth)	BAT-AELs for HCl (mg/Nm³) (1) (2)				BAT-AELs for HF (mg/Nm³)	
	Yearly average or average of samples obtained during one year		Daily average or average over the sampling period		Average over the sampling period	
	New plant	Existing plant (3) (4)	New plant	Existing plant (5)	New plant	Existing plant (5)
<100	1–7	1–15	1–12	1–35	< 1	< 1.5
100–300	1–5	1–9	1–12	1–12	< 1	< 1
≥300	1–5	1–5	1–12	1–12	< 1	< 1

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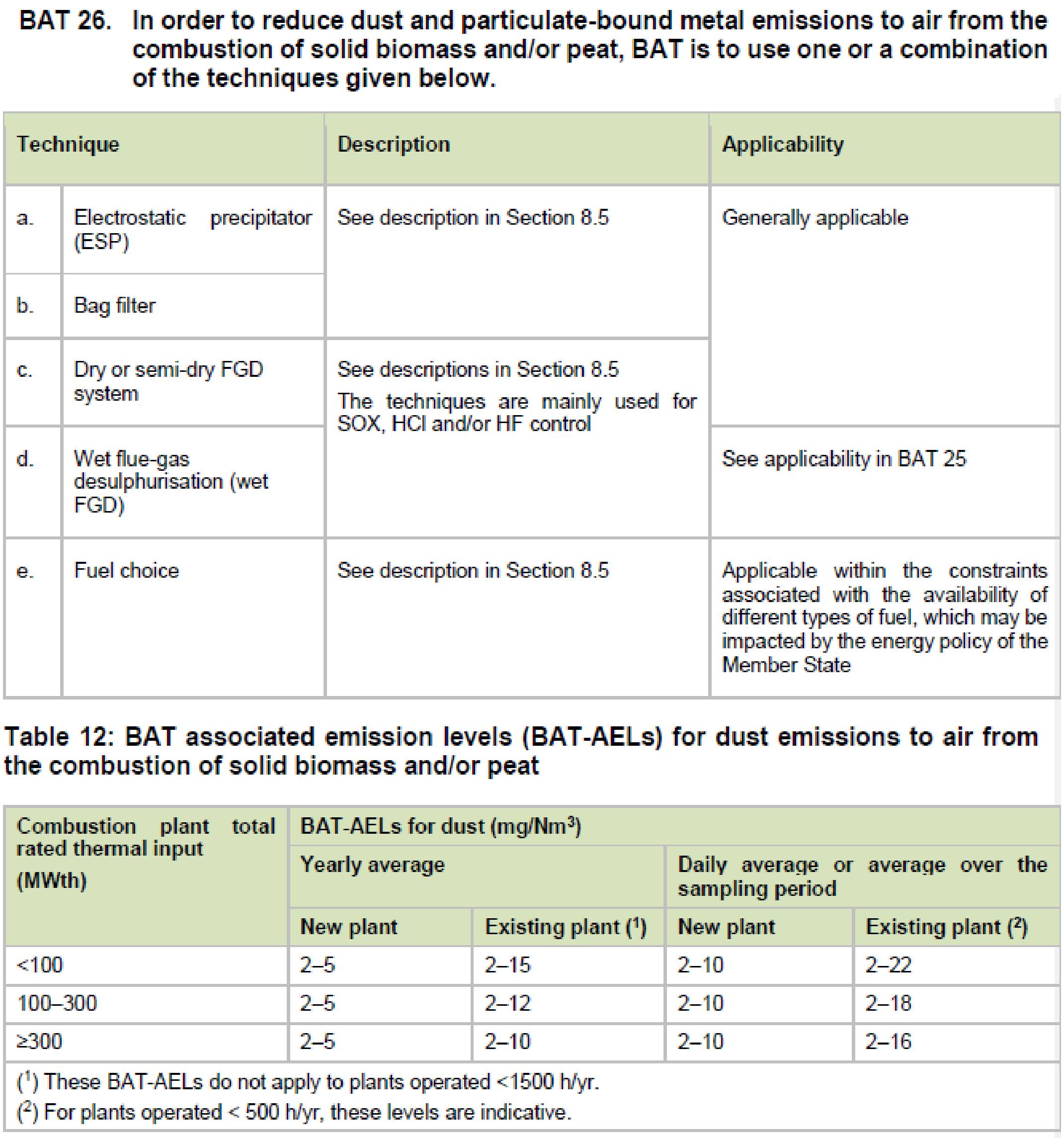
[4] https://consult.environment-agency.gov.uk/psc/permit-reviews-for-food-drink-milk-industries/supporting_documents/Large%20Combustion%20Plant%20OFFICIAL%20LCP%20BATC%20%20Interpretational%20Guidance.pdf



BAT 26. In order to reduce dust and particulate-bound metal emissions to air from the combustion of solid biomass and/or peat, BAT is to use one or a combination of the techniques given below.

Technique		Description	Applicability
a.	Electrostatic precipitator (ESP)	See description in Section 8.5	Generally applicable
b.	Bag filter		
c.	Dry or semi-dry FGD system	See descriptions in Section 8.5 The techniques are mainly used for SOX, HCl and/or HF control	
d.	Wet flue-gas desulphurisation (wet FGD)		See applicability in BAT 25
e.	Fuel choice	See description in Section 8.5	Applicable within the constraints associated with the availability of different types of fuel, which may be impacted by the energy policy of the Member State

Table 12: BAT associated emission levels (BAT-AELs) for dust emissions to air from the combustion of solid biomass and/or peat

Combustion plant total rated thermal input (MWth)	BAT-AELs for dust (mg/Nm^3)			
	Yearly average		Daily average or average over the sampling period	
	New plant	Existing plant (1)	New plant	Existing plant (2)
<100	2–5	2–15	2–10	2–22
100–300	2–5	2–12	2–10	2–18
≥300	2–5	2–10	2–10	2–16

(1) These BAT-AELs do not apply to plants operated <1500 h/yr.

(2) For plants operated < 500 h/yr, these levels are indicative.

129. See guidance point [number not stated in original] *in the general considerations section above on how to address BAT requirements for the application of one, or more, of the techniques specified above. Bag filters are only generally used on biomass plants covered by Chapter IV of the IED due to the different abatement systems used on such plant (e.g. injection of lime and activated carbon that are used to reduce acid gas and heavy metal emissions.). Bag filters are not necessarily BAT for dust abatement for plants that are not covered by Chapter IV of the IED and/or that do not use relevant additional abatement systems.*

NOx and SOx for MEA (excluding SO_3 aerosols)

NOx and SOx level recommendations for MEA in the open literature appear to be based on the following two papers, building on extensive experience by Fluor with their MEA-based Econamine solvent:

a) a paper on the Fluor Econamine FG process (Chapel, 1999)[5],

b) a study by Fluor for IEAGHG (Fluor, 2004)[6].

These papers stated the following:

Chapel (1999) on NOx for MEA: '*Thus far, oxides of nitrogen have never created problems in Econamine FG units, however they have led to corrosion of steel and amine degradation in other plants. The Bridgeport CO_2 recovery plant did not eliminate some corrosion problems until the NOx was reduced to less than 1 ppmv in the absorber feed. NOx is best controlled though control of the peak flame temperature in the boilers. Also, any boiler NOx reduction (SCR) equipment will benefit the absorption process. The chief culprit in NOX is NO_2, which reacts to form nitric acid in the amine solvent and ultimately heat stable salts. However, typically only 10% of the NOx is NO_2 and only a fraction of the NO_2 gas is absorbed in the solvent. NOx can be a problem in the CO_2 product if it is to be used in the food and beverage industry and steps must be taken in the liquefaction unit for its removal.*'

Fluor (2004) on SOx for MEA and MHI and NO_2: '*The flue gas input to a solvent scrubbing unit has to have low concentrations of SOx and NO_2, as these substances result in loss of solvent. The SOx limit is set at 10ppm(v) by Fluor and 1 ppm(v) by MHI. Such low concentrations can be achieved by current FGD technologies. The NO_2 limit set by Fluor is 20 ppm(v) but the selective catalytic reduction (SCR) unit included in the coal fired plants in this study produces a flue gas with a NO_2 concentration to 5 ppm(v).*'

Chapel (1999) on SOx for MEA: '*Flue gases can contain significant concentrations of SOx unless natural gas or very low sulfur fuels are being fired. SOx reacts irreversibly with MEA to produce non-reclaimable corrosive salts that are very detrimental to plant operation. For MEA-based processes, it is less expensive to install a SOx scrubber than to accept the solvent losses when the flue gas contains more than 10 ppmv SO_2. Coal fired boilers produce the highest concentrations of SOx, often 300 to 5000 ppmv before flue gas desulfurization (FGD), but even oil firing can produce 100 ppmv SOx. The limestone or wet lime FGD systems in large power boilers today achieve SOx reductions in the 90-95% range. Therefore, even the flue gas from a low-sulfur liquid or solid fuel, or from a limestone FGD system needs further SO_2 removal. The 10 ppmv SO_2 requirement is met by using the active alkali metal neutralizing agents, caustic soda or soda ash, in a relatively inexpensive spray scrubber.*

Sulfur trioxide, SO_3, presents additional problems. SO_3, like SO_2, leads to solvent losses due to the formation of non-reclaimable heat stable salts, but it also forms a corrosive H_2SO_4

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[5] Chapel, D.G., Mariz, C.L. and Ernest, J. (1999) *Recovery of CO_2 from Flue Gases: Commercial Trends*, Presented at the Canadian Society of Chemical Engineers annual meeting, October 4-6, 1999, Saskatoon, Saskatchewan, Canada. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.204.8298&rep=rep1&type=pdf

[6] Fluor (2004), *Potential for improvement in power generation with post combustion capture of carbon dioxide*, IEAGHG PH4/33, November 2004, https://ieaghg.org/docs/General_Docs/Reports/PH4-33%20post%20combustion.pdf

aerosol in wet scrubbers. Furthermore, less than one-third of the SO_3 may be removed by the SO_2 scrubbing system unless a special mist eliminator is used. Therefore, most of the remaining SO_3 will form heat stable salts in the absorber. The fraction of SOx which forms SO_3 is a function of combustion, fuel composition, and flue gas processing factors, but SO_3 typically accounts for a few percent of the total sulfur. Minimization of SO_3 is a boiler design issue preferably handled upstream of the SO_2 scrubber.'

Oxides of nitrogen – NOx for CESAR1 and nitrosamine management

In CESAR1 testing at TCM[7] on the sensitivity of CESAR1 to NO_2 in the flue gas, which forms nitrosamines that are stable under normal PCC system operating conditions and causes other degradation products, total nitrosamine concentration of up to 4500 mg/kg (0.45% w/w) were observed. The impacts of NO_2 appeared to be able to be reduced by NOx reduction in the power plant, as evidenced by testing for operation with, and the without, the SCR unit on the GT CHP plant at TCM operational.

Specific measures to reduce NO_2, a thiosulphate wash upstream of the PCC unit, were, however, found to have no significant impact in RWE tests on a brown coal plant (Moser, 2023)[8]. But at any level of NOx CESAR1 would require measures to remove or destroy nitrosamines. Moser (2023) noted that "*four tests have been carried out to investigate the degradation rate of CESAR1 and the destruction of nitrosamines in the solvent at elevated desorber pressure of 2.4 bar(a) and corresponding reboiler temperature of 130ºC (for 7 days after 337 day testing time, for further 5 days after 354 days, 7 days after 822 days, and for 12 days after 912 days during the campaign with NO2 removal).*" Total nitrosamines could be maintained at fairly constant levels by these measures but the absolute amounts present were not stated, although detailed measurements were taken, see below:

"*The analyses regarding the nitrosamine concentrations in the solvent have been carried out by HENKEL using in-house analytical methods. The analysis error is estimated at +/-20%. The matrix of the aged solvent means a challenge for the accuracy of the analysis results. For the analysis of the concentration of N-nitrosodiethanolamine (NDELA) the sample preparation comprised the derivation with N-methyl-N-(trimethylsilyl)trifluoracetamide. The measurement is based on gas chromatography (GC) and a chemiluminescence detector after addition of an internal standard (N-nitrosodiisopropanolamine). Results of the double measurement were averaged. Also mononitrosopiperazine (MNPZ) was analysed with GC/chemiluminescence (the response factor was stoichiometrically derived and evaluated against an internal standard). The concentration of total N-nitrosamines comprised the dissociation of the NO group of all nitrosamines in the solvent and detection by chemiluminescence. To compensate*

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[7] Benquet, C., Knarvik, A., Gjernes, E., Hvidsten, O., Romslo, K., and Akhter, S. (2021) *First Process Results and Operational Experience with CESAR1 Solvent at TCM with High Capture Rates*, (ALIGN-CCUS Project) (February 11, 2021). Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021. https://ssrn.com/abstract=3814712 ; http://dx.doi.org/10.2139/ssrn.3814712

[8] Moser, P., Wiechers, G., Schmidt, S., Veronezi Figueiredo, R., Skylogianni, E., Garcia Moretz-Sohn Monteiro, J. (2023) Conclusions from 3 years of continuous capture plant operation without exchange of the AMP/PZ-based solvent at Niederaussem – insights into solvent degradation management, International Journal of Greenhouse Gas Control, Volume 126, 2023. https://doi.org/10.1016/j.ijggc.2023.103894 (https://www.sciencedirect.com/science/article/pii/S1750583623000646)

for matrix interferences the standard addition method was applied, using NDELA for spiking. As the individual nitrosamines in the solvent and their molecular weights are not known the molecular weight of the N–N– – O-group (44 g/mol) as structural element of all nitrosamines is used for the calculation of the mass-related content of total N-nitrosamines. Also here the results of the double measurement were averaged."

Particulates and aerosols[9]

Fine aerosols in flue gases going to amine capture units can lead to very high amine carryover. As flue gases going up the absorber pass the warmest point and start to get cooled by the incoming lean solvent at the top of the absorber they become super-saturated and any aerosol particles present will provide nuclei for small droplets to form. Very small droplets of water and amine are not easily stopped in a water or acid wash because they follow the streamlines of the gas and don't contact any surfaces. So, if an amine 'fog' is produced, amine emissions from the absorber can be very high, perhaps several orders of magnitude, or more, higher than would be achieved with only amine vapour present and well-operated water and acid washes.

There are a number of absorber exit countermeasures proposed for amine aerosols but discussing these, and their merits, is beyond the scope of this report. The alternative, which this report is concerned with because it closely matches existing, proven industrial practice, is stopping aerosols getting to the PCC plant in the first place in significant quantities. Technology Centre Mongstad (TCM) in Norway installed a Brownian filter[10] that successfully removed aerosols after seeing problems with cat cracker flue gases, but this is a specialised unit with a relatively high pressure drop. The National Carbon Capture Centre (NCCC) in Alabama, US, did not use a specialised unit but found that their aerosol issues went away when a baghouse was added[11] to Plant Gaston that supplies their coal flue gas slipstream. This led to the assumption in the field that 'baghouses stop aerosols'.

This simple link is, however, challenged by Toshiba's recent experience with a large PCC pilot on the Mikawa biomass plant in Japan. Despite there being a baghouse in the flue gas path this PCC unit also needs to use, apparently successfully, significant additional absorber exit washing measures to remove an amine aerosol[12]. Obviously fuels are different from the NCCC coal application above and the aerosols may differ (e.g. they may include condensed biomass ash species) and full details of the baghouse and its operation are not published.

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[9] Because of its importance the data in is section was previously published as a LinkedIn article, Baghouses alone don't automatically stop aerosols reaching amine capture plants

[10] Lombardo, G., Shah, M., Fostås, B., Hvidsten, O., Faramarzi, L. de Cazenove, T., Lepaumier, H. and Rogiers, P. (2018) *Results from Testing of a Brownian Diffusion Filter for Reducing the Aerosol Concentration in a Residue Fluidized Catalytic Cracker Flue Gas at the Technology Center Mongstad*, Proc.14th Greenhouse Gas Control Technologies Conference, 21-26 October 2018 (GHGT-14). https://papers.ssrn.com/sol3/papers.cfm?abstract_id=3366032

[11] Morton, F., Anthony, J., Carroll, J., Corser, M., Wu, T. Yongue, R. (2018) *Status of Technology Development at the National Carbon Capture Center*, Proc.14th Greenhouse Gas Control Technologies Conference 21-26 October 2018 (GHGT-14). https://ssrn.com/abstract=3366390

[12] Kitamura, H., Iwasa, K., Fujita, K., Muraoka, D. (2022) *CO_2 Capture Project integrated with Mikawa Biomass Power Plant,* Proc. 16th Greenhouse Gas Control Technologies Conference 23-24 Oct 2022 (GHGT-16). https://ssrn.com/abstract=4282099

Nonetheless, at least circumstantial evidence is there that some combination of additional upstream interventions, possibly providing PAC or hydrated lime particles for SO_3 to condense on as the flue gas goes through the acid dew point, and the nature of the filter cake in the baghouse, with PAC, lime and coal fly ash all present, may be what is required to remove aerosols successfully when using a baghouse in combination with an amine PCC unit.

Hence the suggestion is that new biomass plants plan to install a baghouse rather than an ESP and, if not included already from the outset, provisions are made to add Powdered Activated Carbon (PAC) injection for mercury control and hydrated lime injection for SOx control in case they are found to be necessary to minimise aerosol carryover when the PCC plant is operated.

Conclusions on flue gas cleaning required for the use of MEA or CESAR1 for BECCS

It appears that SOx levels for BREF-compliant biomass plants will generally be below the 10 ppmv (~30 mg/NM^3) recommended value for MEA, but that excursions above this value may occur. Whether or not to use alkali addition in the DCC or, if possible, in the reclaimer seems to be mainly an economic decision.

SOx values are likely to be above the level required for CESAR1 and alkali addition to the DCC is likely to be required. This will also address any HCl and HF present.

BREF-compliant NOx levels, 40-150 mg/Nm^3 (30 – 113 ppmv) would not exceed the 20 ppmv NO_2 guideline for MEA above at an assumed NO2 fraction of 10%, but they would exceed 1 ppmv of NO_2 at even the lowest NOx value of 30 ppmv, notionally corresponding to 3 ppmv NO_2, and reach levels where significant nitrosamine formation (3000 mg/kg in approximately 1 month with 2.35 ppmv NO_2) has been observed in the TCM tests. It is not clear from public-domain evidence what level of nitrosamines could be maintained in the circulating CESAR1 by periodically using elevated temperatures (with 130^{o}C reported in Moser, 2023) in the stripper, since absolute nitrosamine levels were not reported, just a graph showing that the level was held at some level between 50 and 100% of an unstated maximum concentration by using elevated temperatures in the reboiler for periods of 5-12 days.

Because of the need to minimise the risk of aerosols in the flue gas going to any amine capture plant it is suggested that new biomass plants burning any fuel type install a baghouse rather than an ESP for particulate control and, if not included already from the outset, provisions are made to add Powdered Activated Carbon (PAC) injection and hydrated lime injection for SOx control in case they are found to be necessary to minimise aerosol carryover when the PCC plant is operated.

Solvent Degradation: solvent reclaiming or cleaning

In any commercial amine PCC plant the inflow and formation of impurities in the circulating solvent obviously has to be matched, in the long term, by their removal or destruction.

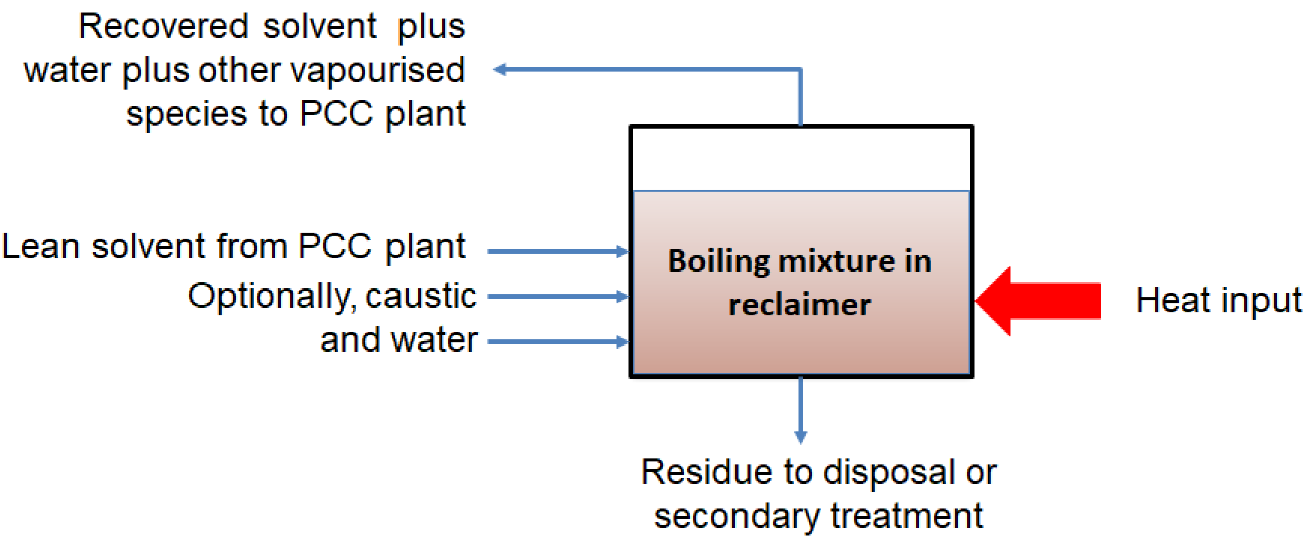
Absolute rates of addition and formation and the level at which techniques for solvent reclaiming or cleaning must be operated can only be determined by very long-term testing under fully-realistic conditions.

But the ability of reclaiming or cleaning techniques to remove the types of impurities likely to be present is obviously extremely important and this ability is determined, to a very large extent, by the fundamental properties of the solvent amines, as will be illustrated in this section.

Thermal reclaiming of MEA and CESAR1 at TCM

Both MEA and CESAR1 have been thermally reclaimed at TCM, using the same equipment and similar methods. These tests constitute a major part of the realistic, public domain information on thermal reclaiming of these solvents and, even though they were not undertaken for solvents on biomass flue gases, the trends that can be inferred for relative behaviour of these two solvents are therefore valuable.

General unsteady-state thermal reclaiming considerations



TCM thermal reclaimer arrangement

In these cases at TCM the reclaimer, arranged as shown above, is operated for a period of time while the PCC plant is running, but in such a way that the amounts of impurities in the circulating solvent are removed at a much faster rate than their rate of addition or formation (and so, to a first approximation, addition and formation during the reclaiming period can be neglected).

The change of the amount of an impurity in the solvent inventory by reclaiming is then given by the formula:

$$\delta C = -C/V.s.\ \delta R$$

Where:

δC is the small amount of the impurity removed in a small solvent volume of δR flowing to the reclaimer

V is the solvent inventory volume$\int$

s is the average selectivity for removal in the reclaimer, from 0 to 1

δR is a small solvent volume flowing to the reclaimer

Expressing in integral form:

$$\int 1/C.dC = - s/V. \int dR$$

And integrating:

$$\ln(C1/C2) = s.R/V$$

or rearranging:

$$s = \ln(C1/C2) / (R/V)$$

$$C2/C1 = e^{(-s.R/V)}$$

Where:

C1, C2 are the initial and final amounts of the impurity

An alternative model is that some fraction of an impurity category has an s value of 1 (i.e. it is not returned to the PCC system, being much less volatile than the solvent constituents) and the remainder, denoted by a mass fraction x, an s value of zero (i.e. it is at least as volatile as the solvent constituents). In this case:

$$C2 = C1.(1-x). e^{(-R/V)} + x.C1$$

Giving:

$$x = [C2 - C1.e^{(-R/V)}] / [1- e^{(-R/V)}]$$

Comparison between reclaiming trends for MEA and CESAR1 at TCM and implications for thermal reclaiming effectiveness

Unsteady-state thermal reclaiming with a running PCC plant have been undertaken at TCM for both MEA[13] and CESAR1[14]. The reported results and analyses for key processing variables are shown in the table below.

As can be seen, in MEA reclaiming there is a high selectivity for removal of all the categories of impurities; clearly virtually none are returned to the PCC system with the vapour from the reclaimer.

In CESAR1 reclaiming, however, on average ~60% of the ‘degradation products’ in the lean solvent feed to the reclaimer, about 40% of the metals and about 50% of the heat stable salts appear to be returned with the amine and water vapour each time a batch of the solvent is reclaimed. In fact, though, since none of these impurity classifications are a single species, but rather a very heterogeneous mixture, the behaviour may perhaps be better described as a combination of material with much higher (i.e. approaching 1) and much lower (approaching zero) removal selectivities, for different species. Assuming this latter model, unremovable fractions in the first TCM CESAR1 reclaiming run are 15.1% for degradation products, 3.9% for metals and 10% for HSS, rising for the first two categories to 17.1% and 6% respectively in the second reclaiming run, with unremovable HSS staying at 10%. Insufficient details are provided to confirm this hypothesis, but it might be expected that if certain species are not removed in reclaimed or subject to further degradation then would accumulate over time, as do the unremovable fractions of the degradation products and metals categories in the table below.

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[13] Flø, N., Faramarzi, L., de Cazenove, T., Hvidsten, O., Morken, A., Hamborg, E., Vernstad, K., Watson, G., Pedersen, S., Cents, T., Fostås, B., Shah, M., Lombardo, G. and Gjernes E. (2017*)* *Results from MEA Degradation and Reclaiming Processes at the CO_2 Technology Centre Mongstad*, Energy Procedia, Volume 114, Pages 1307-1324, http://www.sciencedirect.com/science/article/pii/S1876610217321021

[14] Campbell, M., Akhter, S., Knarvik, A., Muhammad, Z., and Wakaa, A. (2022) *CESAR1 Solvent Degradation and Thermal Reclaiming Results from TCM Testing,* Proc. 16th Greenhouse Gas Control Technologies Conference (GHGT-16), 23-24 Oct 2022. https://ssrn.com/abstract=4286150 or http://dx.doi.org/10.2139/ssrn.4286150

Reported TCM thermal reclaiming data and estimated selectivities for removal

		Degradation products	Metals	HSS
MEA reclaiming, R/V	3[15]			
Expected reduction for s=1	96.02%			
Oct-15 reclaiming run after 1843 hrs operation – reduction from reclaiming		~95%	>95%	>95%
Apparent selectivity for removal (for 95%)		0.9986	0.9986	0.9986
CESAR1 reclaiming, R/V	4.5			
Expected reduction for s=1	98.98%			
Apr-20 reclaiming run after ~1600 hrs operation – reduction from reclaiming		84%	95%	89%
Apparent selectivity for removal		0.4072	0.6657	0.4905
Unremovable fraction, x		15.1%	3.9%	10.0%
Oct-20 reclaiming run after ~2200 hrs operation		82%	93%	89%
Apparent selectivity for removal		0.3811	0.5909	0.4905
Unremovable fraction, x		17.1%	6.0%	10.0%

These reclaiming tests are the main body of information available in the open literature, but they have a number of limitations for extrapolation to any commercial plant operation:

- The flue gases, and hence impurity types and amounts, will obviously be specific to that plant
- The operating regime will also be specific
- Very seriously, the operating period for a commercial PCC plant will be ~8000 hrs/yr and the plant is likely to be running for at least a year between major planned outages and perhaps much longer, and for likely over a decade in total – the few thousands of hours running above, although typical of pilot testing, is far too short to give a reliable prediction of even the first year's trends

Nonetheless, it appears likely that all or most of the impurities likely to be found when using MEA as a post-combustion capture solvent can be almost entirely removed by simple thermal reclaiming, whereas some fraction of the impurities found when using CESAR1 cannot. More exact conclusions and, most importantly, the implications for plant operation, would need fully representative testing for a period of 12-24 months.

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[15] In (Flø, 2017) it was incorrectly stated that "A total accumulated amount of 46 000 kg solvent was fed to the reclaimer during the whole period of 3 days. This corresponds to about 110 % of the total solvent inventory." But this is inconsistent with the average flow shown in Figure 6, which averages around 2000 kg/h over 3 days, so roughly 3 x 24 x 2000 = 144 000 kg. After correspondence on the matter TCM confirmed by email that "the solvent flow to the reclaimer over the 3 days was 143 570 kg. This is 3 times the inventory."

Moser (2023) also found similar, but probably (impurity categories are different) slightly better, results for partial removal of impurities from CESAR1 by cleaning using ion exchange and was able to run for an extended period of 40 months:

Reduction of the concentrations of contaminants in the CESAR1 solvent
by the application of anion and cation exchange

Concentrations	Fe	Ni	chloride	nitrate	sulfate	formate	acetate	glycolate	oxalate	propionate
	[mg/kg]	[mg/kg]	[mg/kg]	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[wt.%]
Before cation/anion exchange	11	4	60	0.16	0.076	0.37	0.27	0.089	0.12	0.077
After cation/anion exchange	3	0	<5	0.023	0.0054	0.061	0.036	0.005	0.0076	0.005
Reduction [%]	73	100	92	86	93	84	87	94	94	94

The same pilot plant has also used ion exchange for MEA cleaning, with apparent success although the period for testing satisfactory operation after reclaiming (approximately 100 days) had been exceeded when running fresh solvent with no reclaiming (Weir, 2023)[16].

Solvent reclaiming/cleaning conclusions for the use of MEA or CESAR1

It appears that MEA can be thermally reclaimed with very high rejection of all impurities. In the public-domain example cited the reclaimer was operated intermittently but in commercial plants (e.g. Pentair[17], Bechtel[18]) it is likely that MEA reclaiming will take place continuously. The reclaimer, or at least the first stage of reclaiming, may be vented into the stripper for full energy recovery, allowing reclaiming at very high rates (e.g. up one inventory volume per week) with limited penalties on plant output. Ion exchange cleaning has been used for MEA operation but, given the efficacy of thermal reclaiming for MEA, seems unlikely to be the preferred option.

CESAR1 has been operated satisfactorily for limited periods (total 3800 hours reported) with thermal reclaiming, but of the order of 10% of impurities seem unable to be removed by this method and the build-up of these compounds over the longer term is therefore a possibility. Somewhat better levels of impurity removal, but still not complete, appear to be feasible with ion exchange cleaning and longer periods of satisfactory operation (>3 years), with appreciable levels of impurities present, have been demonstrated using this method (with also some level of solvent make-up). There is a caveat here, though, in that this is at a single plant (RWE

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[16] Weir, H., Sanchez-Fernandez, E., Charalambous, C., Ros, J., Garcia Moretz-Sohn Monteiro, J., Skylogianni, E., Wiechers, G., Moser, P., van der Spek, M., Garcia, S. (2023) *Impact of high capture rates and solvent and emission management strategies on the costs of full-scale post-combustion CO2 capture plants using long-term pilot plant data*, International Journal of Greenhouse Gas Control, Volume 126. https://doi.org/10.1016/j.ijggc.2023.103914, https://www.sciencedirect.com/science/article/pii/S1750583623000841 (see also for open-access https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4144048)

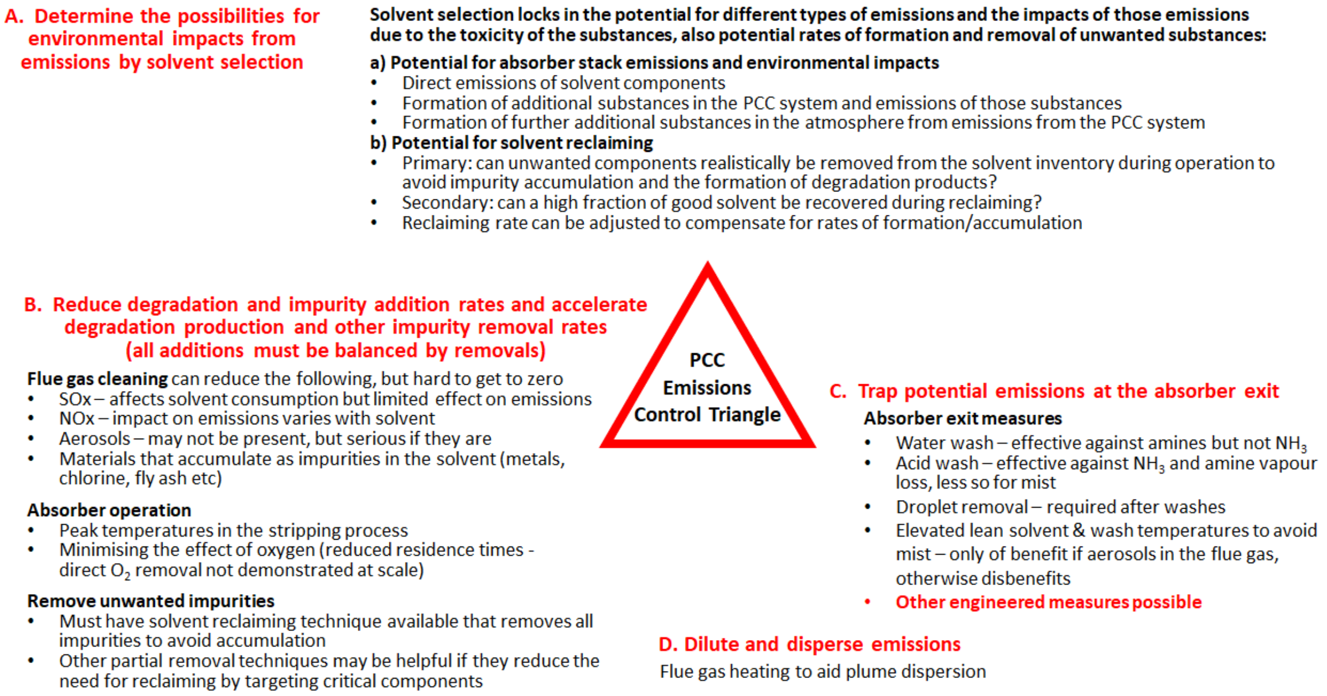
[17] https://carboncapture.pentair.com/en/solutions/cc-product-low-purity-advanced-amine-capture-plants

[18] https://ukccsrc.ac.uk/open-access-sherman-feed/

Niederaussem) and the fly ash at this plant has been demonstrated to have beneficial effects with respect to amine solvent degradation[19].

Solvent Degradation: acid wash for amine and degradation product emissions control

General considerations



A. Determine the possibilities for environmental impacts from emissions by solvent selection

Solvent selection locks in the potential for different types of emissions and the impacts of those emissions due to the toxicity of the substances, also potential rates of formation and removal of unwanted substances:

a) Potential for absorber stack emissions and environmental impacts
- Direct emissions of solvent components
- Formation of additional substances in the PCC system and emissions of those substances
- Formation of further additional substances in the atmosphere from emissions from the PCC system

b) Potential for solvent reclaiming
- Primary: can unwanted components realistically be removed from the solvent inventory during operation to avoid impurity accumulation and the formation of degradation products?
- Secondary: can a high fraction of good solvent be recovered during reclaiming?
- Reclaiming rate can be adjusted to compensate for rates of formation/accumulation

B. Reduce degradation and impurity addition rates and accelerate degradation production and other impurity removal rates (all additions must be balanced by removals)

Flue gas cleaning can reduce the following, but hard to get to zero
- SOx – affects solvent consumption but limited effect on emissions
- NOx – impact on emissions varies with solvent
- Aerosols – may not be present, but serious if they are
- Materials that accumulate as impurities in the solvent (metals, chlorine, fly ash etc)

Absorber operation
- Peak temperatures in the stripping process
- Minimising the effect of oxygen (reduced residence times - direct O_2 removal not demonstrated at scale)

Remove unwanted impurities
- Must have solvent reclaiming technique available that removes all impurities to avoid accumulation
- Other partial removal techniques may be helpful if they reduce the need for reclaiming by targeting critical components

C. Trap potential emissions at the absorber exit

Absorber exit measures
- Water wash – effective against amines but not NH_3
- Acid wash – effective against NH_3 and amine vapour loss, less so for mist
- Droplet removal – required after washes
- Elevated lean solvent & wash temperatures to avoid mist – only of benefit if aerosols in the flue gas, otherwise disbenefits
- **Other engineered measures possible**

D. Dilute and disperse emissions

Flue gas heating to aid plume dispersion

As shown in the figure above, many interacting factors affect atmospheric emissions. But to prevent amine and ammonia emissions an acid wash at the absorber exit is the only tested option that will ensure very low emissions, although other measures may reduce the load on the acid wash and have some effect on exit emission levels.

Acid wash test results for both MEA and CESAR1 are available, although unfortunately not on the same plant for direct comparison. Details are summarised below.

MEA with acid wash

For an example of an acid wash on a PCC pilot plant, for which data is available, see (Khakaria, 2014)[20]. TNO’s 6 tCO_2/day /0.65 m diameter capture plant then in place at Maasvlakte had an acid wash column added using 1.26 m of Sulzer Mellapak 250 structured

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[19] Buvik, V., Vevelstad, S., Moser, P., Wiechers, G., Wanderley, R., Garcia Moretz-Sohn Monteiro, J., Knuutila, H. (2023) *Degradation behaviour of fresh and pre-used ethanolamine*, Carbon Capture Science & Technology, Volume 7. https://doi.org/10.1016/j.ccst.2023.100110 ; https://www.sciencedirect.com/science/article/pii/S2772656823000143

[20] Khakharia, P., Huizinga, A., Lopez, C., Sanchez, C., Mercader, F., Vlugt, T. & Goetheer, E. (2014) *Acid Wash Scrubbing as a Countermeasure for Ammonia Emissions from a Postcombustion CO2 Capture Plant*, Ind. Eng. Chem. Res. 53, 13195−13204. https://pubs.acs.org/doi/pdf/10.1021/ie502045c

packing with a liquid distributor followed by a demister (KnitMesh - Sulzer Chemtech) to prevent carryover of droplets. The demister was capable of removing droplets of 2 μm with 96.4% efficiency, and above 10 μm with 100% efficiency. Overall increase in column height required for the acid wash was estimated to be 4.7 m for a full-size column design.

Typical NH_3 emissions at the water wash outlet were in the range of 15−20 mg/Nm^3 under normal operation with MEA, but additional ammonia (up to 150 mg/Nm^3) was added for test purposes. Experimental results showed ammonia emissions below 5 mg/Nm^3 at a pH of 6 for both normal and added NH_3 conditions. MEA emissions after the acid wash were in the range 1−3 mg/Nm^3, mostly below 1 mg/Nm^3, from water wash outlet values of 1.2−26.8 mg/Nm^3 (but generally below 10 mg/Nm^3).

CESAR1 with an acid wash

CESAR1 test data with an acid wash comes from trials at TCM[21,22], using a gas turbine exhaust gas (TCM CHP flue gas). The results were compared with MEA testing that, significantly for the comparisons, did not use an acid wash.

‘*Formaldehyde, acetaldehyde, and acetone concentrations were determined by extractive sampling. The data for the flue gas after the absorber are shown in the table below.’*

Depleted flue gas aldehyde/ketone concentrations

#	Formaldehyde, mg/Sm^3	Acetaldehyde, mg/Sm^3	Acetone, mg/Sm^3
3	0.0635	0.0931	1.14
7	0.0406	0.0596	1.42
11	0.0546	0.0801	2.85
15	0.0190	0.0279	1.13

It was noted that “*Acetone levels measured during the MEA tests were sufficiently low at or below the detection limit of 1 mg/Sm^3, while with CESAR-1 they were measurable at between 1–3 mg/Sm^3 even though the upper water wash was configured as an acid wash for these tests and not in the MEA campaign“.*

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[21] https://gassnova.no/app/uploads/sites/5/2022/04/10-CESAR-1-Solvent.pdf

[22] Hume, S., Shah, M., Lombardo, G. and Kleppe, E. (2021) *Results from CESAR-1 testing with combined heat and power (CHP) flue gas at the CO2 Technology Centre Mongstad*, TCCS-11 - Trondheim Conference on CO2 Capture, Transport and Storage, Trondheim, Norway - June 21–23, 2021. https://sintef.brage.unit.no/sintef-xmlui/bitstream/handle/11250/2786512/Results%20from%20Cesar-1%20Testing%20with%20Combined%20Heat%20and%20Power%20%28CHP%29%20Flue%20Gas%20at%20the%20CO2%20Technology%20Centre%20Mongstad.pdf

As a partial comparison, acetaldehyde levels of about 0.3 ppmv (~0.6 mg/Sm^3) were observed in operation with MEA at TCM[23] when capturing from RFCC flue gas and prior to the solvent becoming heavily degraded.

TCM also measured final flue gas concentrations of solvent components (AMP and PZ) along with ammonia during the CESAR1 testing, as shown below.

Depleted flue gas stream ammonia and solvent component concentrations

#	AMP, mg/Sm^3	PZ, mg/Sm^3	Ammonia, mg/Sm^3
4	0.06	0.01	0.04
5	0.04	<0.007	0.03
9	0.03	<0.007	0.02
13	0.03	<0.007	0.03

Comments on these results were, "*The solvent components of CESAR-1 appear to show higher vapor pressure than is associated with MEA solvent, which was previously measured by an external contractor at 0.006 mg/Sm3 during testing on CHP flue gas. PZ was barely detected, only showing up in Test 4, which shows that perhaps a longer extraction sample period would help to improve determination of this species at the ppb level.*

It was also noted that ,*"Ammonia levels are far lower than the previous MEA CHP tests results, measured at 13 mg/Sm^3, suggesting that ammonia does not represent a significant degradation product of CESAR-1."* but since the MEA tests were without the acid wash this comparison is not fully evidenced.

Acid Wash conclusions for the use of MEA or CESAR1

An acid wash can be used effectively with both MEA and CESAR1 and will generally reduce alkaline species, principally amines and ammonia, down to less than 1 mg/m^3. Slight differences between the solvents may remain:

- AMP emissions from CESAR1 may be higher than MEA or PZ emissions
- NH_3 emissions from MEA may be higher than from CESAR1, although typically less than 1 mg/m^3 after an acid wash
- Acetone, which will not react with the acid, is likely to be emitted at higher levels from CESAR1
- Acetaldehyde emissions are likely to be higher from MEA

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[23] Morken, A.K., Pedersen, S., Kleppe, E.R., Wisthaler, A., Vernstad, K., Ullestad, Ø., Flø, N.E., Faramarzi, L. and Hamborg, E. (2017) *Degradation and Emission Results of Amine Plant Operations from MEA Testing at the CO_2 Technology Centre Mongstad*, Energy Procedia, Volume 114, 2017, Pages 1245-1262, https://doi.org/10.1016/j.egypro.2017.03.1379 ; http://www.sciencedirect.com/science/article/pii/S1876610217315643

A more representative comparison between emissions from the two solvents with an acid wash would require back-to-back long term tests on the relevant flue gas that also include commercially-relevant reclaiming for each solvent. Such test data does not appear to be available in the public domain (and such tests may not have been conducted).

CO_2 capture rate and regeneration energy requirements

Public domain capture rate and regeneration energy data for comparison between MEA and CESAR1 is taken from the following sources. These were selected because they were from experienced and well established pilot facilities, test data in the same equipment and under similar conditions was available for the other solvent, and an extensive body of data was available rather than isolated results. These TCM and RWE facilities had also intended these tests to allow a comparison between these two solvents.

MEA capture rate and regeneration energy data sources

A. Technology Centre Mongstad

Shah, M., Lombardo, G., Fostås, B.,Benquet, C., Morken, A. and de Cazenove, T. (2018) *CO_2 Capture from RFCC Flue Gas with 30w% MEA at Technology Centre Mongstad*, *Process Optimization and Performance Comparison.* 14th Greenhouse Gas Control Technologies Conference Melbourne October 21-26, 2018 (GHGT-14). https://ssrn.com/abstract=3366149 ; http://dx.doi.org/10.2139/ssrn.3366149

Shah, M., Silva, E., Gjernes, E. and Åsen, K. (2021) *Cost Reduction Study for MEA based CCGT Post-Combustion CO_2 Capture at Technology Center Mongstad*, Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021. https://ssrn.com/abstract=3821061 ; http://dx.doi.org/10.2139/ssrn.3821061

B. RWE Niederaussem Pilot Plant

Weir, H., Sanchez-Fernandez, E., Charalambous, C., Ros, J., Garcia Moretz-Sohn Monteiro, J., Skylogianni, E., Wiechers, G., Moser, P., van der Spek, M., Garcia, S. (2023) *Impact of high capture rates and solvent and emission management strategies on the costs of full-scale post-combustion CO2 capture plants using long-term pilot plant data*, International Journal of Greenhouse Gas Control, Volume 126. https://doi.org/10.1016/j.ijggc.2023.103914, https://www.sciencedirect.com/science/article/pii/S1750583623000841 (see also for open-access https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4144048)

C. National Carbon Capture Center pilot plant

Morgan, R. (2017) *Physical Property Modeling of Solvent-Based Carbon Capture Processes with Uncertainty Quantification and Validation with Pilot Plant Data*, PhD thesis, West Virinia University. https://researchrepository.wvu.edu/etd/6262/

CESAR1 capture rate and regeneration energy data sources

A. Technology Centre Mongstad

Benquet, C., Knarvik, A., Gjernes, E., Hvidsten, O., Romslo, K., and Akhter, S. (2021) *First Process Results and Operational Experience with CESAR1 Solvent at TCM with High Capture Rates*, (ALIGN-CCUS Project) (February 11, 2021). Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021. https://ssrn.com/abstract=3814712 ; http://dx.doi.org/10.2139/ssrn.3814712

Hume, S., Shah, M., Lombardo, G. and Kleppe, E. (2021) *Results from CESAR-1 testing with combined heat and power (CHP) flue gas at the CO2 Technology Centre Mongstad*, TCCS-11 - Trondheim Conference on CO2 Capture, Transport and Storage, Trondheim, Norway - June 21–23, 2021. https://sintef.brage.unit.no/sintef-xmlui/bitstream/handle/11250/2786512/Results%20from%20Cesar-1%20Testing%20with%20Combined%20Heat%20and%20Power%20%28CHP%29%20Flue%20Gas%20at%20the%20CO2%20Technology%20Centre%20Mongstad.pdf

Hume, S., McMaster, B., Drageset, A., Shah, M., Kleppe, E. and Campbell, M. (2022) Results from CESAR1 Testing at the CO_2 Technology Centre Mongstad. Verification of Residual Fluid Catalytic Cracker (RFCC) Baseline Results, Proceedings of the 16th Greenhouse Gas Control Technologies Conference (GHGT-16) 23-24 Oct 2022. https://ssrn.com/abstract=4280571 ; http://dx.doi.org/10.2139/ssrn.4280571

B. RWE Niederaussem Pilot Plant

Weir (2023), as above for MEA

Comparison of capture rate and regeneration energy data

A. Tests on TCM CHP flue gas, ~3.5-3.7% v/v CO_2

The minimum flue gas temperature was 40°C with CESAR1 solvent because of precipitation at lower temperature in the absorber, while it was 30°C in MEA case. It was easy to reverse the precipitation by flushing the absorber with hot solvent at high flow rate, but this might be not optimal for a full-scale plant. The flue gas temperature strongly influences the steam consumption.

TCM run series	%w/w MEA in water	Capture rate	Packing height (m)	SRD (GJ/tCO2)
MEA				
MEA-3	43%	86%	18	3.6
F2	36%	90%	18	3.8
B3-rep	37%	91%	18	3.6
D3-rep	36%	97%	24	3.7
CESAR1				
K		85%	18	3.5
C		90%	18	3.4
D		98%	18	3.9
K		85%	24	3.3
AA		90%	24	3.5
BB		98%	24	3.75
Hume (2021)		~96%	24	~3.45 minimum*

* See table below for range of (Hume, 2021) test data. Higher values are ascribed to foaming in the stripper.

#	Heat Duty, MJ/hr	Product CO_2 Flow, kg/hr	Specific Thermal Use, GJ/t-CO_2	Captured CO_2, kg/hr	Specific Thermal Use, GJ/t-CO_2
1	17,329	5014	3.46	5075	3.41
2	17,403	5045	3.45	5049	3.45
3	17,434	5023	3.47	5049	3.45
4	17,562	5009	3.51	5045	3.48
5	18,097	4969	3.64	5003	3.62
6	18,103	4952	3.65	4990	3.63
7	18,046	4928	3.66	4975	3.63
8	18,081	4941	3.66	4971	3.64
9	18,839	4928	3.82	4963	3.80
10	18,863	4927	3.83	4960	3.80
11	19,148	4948	3.87	4919	3.89
12	18,872	4883	3.86	4891	3.86
13	17,692	5005	3.53	5098	3.47
14	17,683	4994	3.54	5099	3.47
15	17,730	5008	3.54	5110	3.47
16	17,751	5017	3.54	5117	3.47

B. Tests on TCM RFCC flue gas, 13-14% v/v CO_2

TCM run series	%w/w MEA in water	Capture rate	Packing height (m)	SRD (GJ/tCO2)
MEA (Shah, 2018)				
1A-1	30%	90.5%	18	3.5
1A-2	30%	89.4%	18	3.54
CESAR1 (Hume, 2022)				
EPRI Baseline		91%	18	3.23
B4REP2		89.6%	18	3.06
B1		89.5%	18	3.13

C. RWE Niederaussem tests, ~15% v/v CO_2

Tests results at Niederaussem were summarised into expected plant performance by Weir (2023) as:

TCM run series	%w/w MEA in water	Capture rate	Packing height (m)	SRD (GJ/tCO2)
MEA (Weir, 2023)				
MEA 90%	30%	90%	18	3.6
CESAR1 (Weir, 2023)				
CESAR1, 90%		90%	28*	3.0
CESAR1, 95%		95%	28*	3.0
CESAR1, 98%		98%	28*	3.24

* Including dry bed for amine emission reduction

D. National Carbon Capture Center tests – ~30%w/w MEA, ~10.3% v/v CO_2*

Case No.	Capture rate (gas data)	L/G (w/w)	Lean loading (mole CO_2/MolMEA)	Rich loading (mole CO_2/ MolMEA)	SRD (GJ/tCO_2)	Number of beds (Inter-coolers)
K15	99.4%	3.042	0.224	0.413	3.81	3 (2)
K14	98.3%	3.055	0.224	0.42	3.86	3 (2)

* These tests were undertaken as part of generated a pre-determined matrix of conditions for model calibration, i.e. they were not optimised high capture rate tests, as suggested by the relatively high lean loadings and low rich loadings. Packing bed height is 6 m, i.e. 18 m total.

Capture rate and regeneration energy conclusions for the use of MEA or CESAR1

Based on the trends from the test series of multiple individual operating condition points at TCM (supported by the published NCCC data for MEA) it appears that both MEA[24] and CESAR1 can achieve capture rates above 95% of the CO_2 in the flue gas with similar amounts of packing in the absorber (except, possibly, for an additional dry bed for CESAR1).

Specific reboiler duties for CESAR1 vs 30% w/w MEA are at best (RWE tests overall summary, coal flue gas) 15% lower for CESAR1, but may be 8 -13% lower (TCM data, RFCC flue gas). This difference would be less if compared to 35% w/w MEA, since this has slightly better energy performance, but no data has been identified for higher-CO_2 flue gases.

For TCM tests on GT (CHP) flue gas CESAR1 reboiler duties are 0-7% lower than 35% w/w MEA data based on the reported test data.

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[24] The TCM D3-rep 97% capture point for MEA is consistent with trends for the whole series of 8 operating condition points in this test series and was repeated in duplicate separate tests at the optimum operating conditions. It is also consistent with the published data for MEA at high capture rates from NCCC.

OVERALL CONCLUSIONS

Key characteristics for MEA and CESAR1 (or any solvent used for post-combustion capture)

These fall into two categories, showstoppers and marginal improvements (scope for cost reduction), with some in between.

An essential *caveat*, that will be repeated, is that all of these characteristics can only be reliably quantified after long-duration operational experience in full-scale plants and even then only for the specific applications for which multiple examples exist. Pilot testing can also give an indication of likely characteristics but needs to be on the specific flue gas, to incorporate all the relevant features of the proposed commercial plant, including actual solvent management and emissions control techniques, and to be conducted for at least a year to give time for solvent composition to stabilise and factors such as climatic variations and normal plant ‘upsets’ to come into play.

Key characteristics include:

a) Showstoppers:

- Emissions to atmosphere
- Emissions to water
- Operator health and safety
- Uneconomic project – higher-than-expected running costs that are in excess of revenues
- Uneconomic project – unexpected maintenance costs making capital recovery or even operation unviable

b) Marginal improvements (scope for cost reduction):

- Reduced equipment sizing / lower-cost materials
- Reduced solvent make-up and waste disposal costs
- Improved equipment performance – e.g. better capture rates, reduced energy requirements
- Reduced financing costs since lower project risk premium

c) In-between issues:

- Process upsets triggering closure – could exceed annual emission allowances in short period
- Corrosion – reduced equipment lifetime or increased waste disposal costs – catalytic effect on degradation
- Solvent inventory or waste streams may be hazardous material

Comparison of MEA and CESAR1 on showstopper issues

Emissions to atmosphere from both solvents can be reduced to low levels by the addition of an acid wash and, for CESAR1, possibly also a ‘dry bed’ at the top of the absorber. Relatively high acetone emissions from CESAR1 cannot, however, be stopped by an acid wash; conversely acetaldehyde emissions from MEA appear to be relatively high. PCC project environmental performance assessments that show impacts below AELs for toxic conversion products such as nitrosamines are in the public domain for MEA[25] but no similar studies for CESAR1 have been identified.

Emissions to water are not expected directly but may occur via deposition of stack emissions, possibly after solution in water droplets in the stack plume, or as a result of upsets in solvent handling, including in the supply chain. The assessment by NETL presented earlier in this report suggest that CESAR1 would present a higher risk.

Operator health and safety appears to present more challenges with CESAR1 than MEA, again based on the NETL assessment and, in particular, the management of nitrosamines, potent cancer-causing chemicals, needs to be resolved for CESAR1. Nitrosamine management for MEA would be achieved by a high level of thermal reclaiming to remove possible degradation product nitrosamine precursors and probably to remove or thermally destroy any nitrosamines present (although this approach does not appear to have been verified by publicly-available data). CESAR1 readily forms stable nitrosamines with the NO_2 that will be present in flue gases. It has been proposed (Moser, 2023) that nitrosamine levels in circulating CESAR1 can be controlled by periodically increasing the temperature in the reboiler to 130°C for 5-12 days at a time but, although measured, the absolute concentrations of nitrosamines that were achieved using this approach were not reported.

Uneconomic project – higher-than-expected running costs that are in excess of revenues – Based on limited full-scale operational experience this is probably most likely to occur because of unexpectedly-high solvent management costs. As noted, for meaningful comparisons between MEA and CESAR1 fully-representative test data is required. The scope for high solvent management costs on commercial projects is illustrated in the figure below that shows a Global CCS Institute analysis of PCC costs for Boundary Dam Unit 3 (BD3), Petra Nova and a proposed (but not built) plant at Shand. The ‘Variable O&M’ values, particularly for

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[25] For an example of UK ongoing experience of air quality impact assessments for amine releases from capture plants see the Keadby CCGT+PCC project permitting page: https://consult.environment-agency.gov.uk/psc/dn17-3ef-keadby-generation-limited-v011/ and specifically, for routine operation stack emissions: Environmental Statement Volume II - Appendix 8C: Air Quality Assessment of Amine Degradation Products and for major unplanned emissions: Document 6.2.18 - ES Chapter 18 - Major Accidents and Disasters 070921

Also for the Net Zero Teesside CCGT+PCC project, here: https://consult.environment-agency.gov.uk/psc/ts10-5qw-net-zero-teesside-power-north-sea-storage/ Environmental Risk Assessment and Supporting Info - Appendix F - Air Impact Assessment Model input data files for noise and air quality modelling

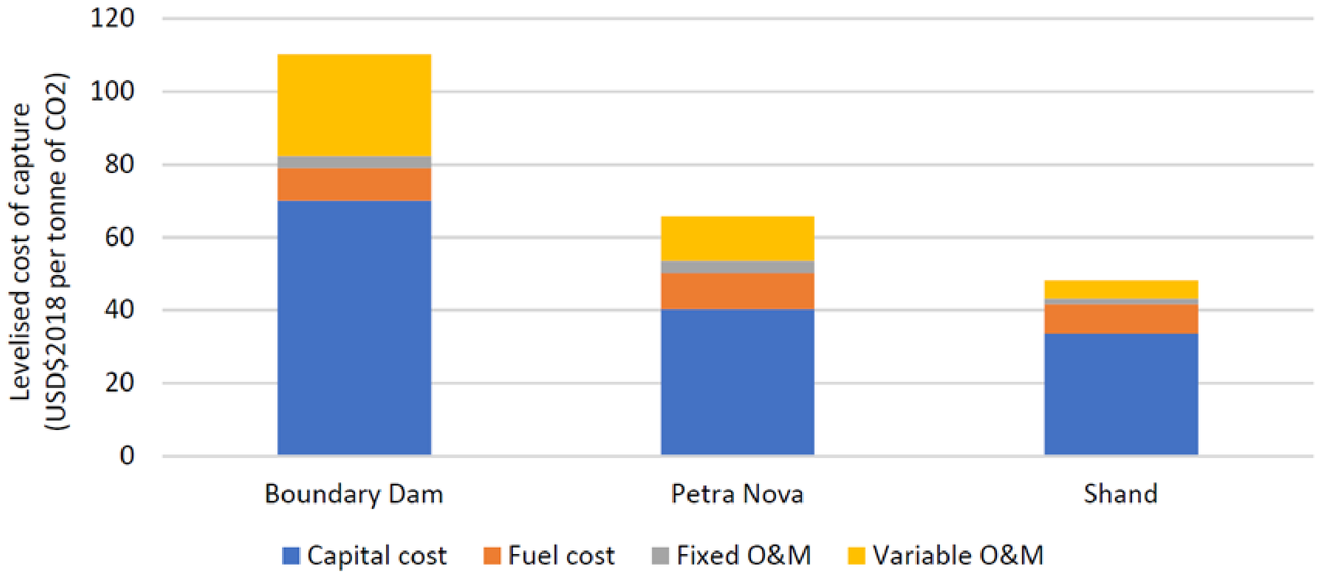
For a smaller Energy-from-Waste (EfW) plant with PCC, for Suez on Teesside see: https://www.developmentmanagement.stockton.gov.uk/online-applications/applicationDetails.do?activeTab=documents&keyVal=ROQF1UPK03400 ES VOLUME 2_APPENDICES PART4

BD3, are very high and, as confirmed by evidence to a Saskatchewan parliamentary committee[26], were, at least for several years, perhaps up to four times the amount per tonne of CO_2 captured than was expected (and much higher that the extra fuel costs for meeting the additional energy requirements of the PCC plant). Commercial PCC projects with mixed amines may now be using specialized reclaiming facilities to clean up their solvent inventories, and possibly stored dirty solvent, on an annual, or more frequent, basis, although some level of impurities may build up in the intervals between these reclaiming campaigns. But no information is in the public domain.

GCCSI analysis of levelized cost of capture for BD3, Petra Nova and a proposed retrofit plant at Shand Data from GCCSI, Global Status of CCS Report, 2019; 'Variable O&M' costs are likely to be predominantly for solvent management and replacement.

Results based on 8% discount rate, 30 years' project life, 2.5 years' construction time, capacity factor of 85%. Cost data are normalized to 2017 values. Stated expected accuracy range: Boundary Dam and Petra Nova: -10% to +15%, Shand: -25% to +40%.

See also http://docs.legassembly.sk.ca/legdocs/Legislative%20Committees/CCA/Tableddocs/CCA%2061-28%20SaskPower%20Responses%20to%20questions%20raised%20at%20the%20June%2027,%202018%20meeting.pdf



Uneconomic project – unexpected maintenance costs making capital recovery or even operation unviable. No examples of this appear to exist in the very limited number of projects to date. Experience suggests that both MEA and CESAR1 can be operated in PCC pilot units with stainless steel or similar construction without undue maintenance requirements.

Comparison of MEA and CESAR1 on marginal improvements (scope for cost reduction)

Reduced equipment sizing / lower-cost materials – Based on pilot testing (i.e. no FEED studies using CESAR1 have been identified) both equipment sizing (e.g. main vessel sizes) and construction materials (stainless steels or similar) appear to be similar for MEA and CESAR1. Minor differences may exist, e.g. possibly an extra dry bed in the absorber for

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[26] https://docs.legassembly.sk.ca/legdocs/Legislative%20Committees/CCA/Tableddocs/CCA%2061-28%20SaskPower%20Responses%20to%20questions%20raised%20at%20the%20June%2027,%202018%20meeting.pdf

CESAR1, slightly smaller reboiler units for CESAR1, but given the relatively small differences in specific reboiler duties indicated by the test data presented in this report (i.e. a range 0-15% less in reboiler duty for CESAR1 vs MEA in conventional PCC systems) these equipment differences must be limited in magnitude.

Reduced solvent make-up and waste disposal costs – as already noted, fully-representative long-term tests are needed to determine the actual performance of a solvent in a particular application. Based on experience in the RWE Niederaussem pilot (Weir, 2023) suggested potentially higher costs for managing the more expensive CESAR1 solvent, but it must be emphasised that no meaningful data for either solvent has been identified for commercial BECCS PCC operation and this will therefore be covered by examining sensitivity ranges in the forthcoming techno-economic analysis (TEA) report.

Improved equipment performance – e.g. better capture rates, reduced energy requirements. Based on the pilot plant performance data presented in this report MEA and CESAR1 appear very similar in respect of achievable capture rates and the packing height required. Energy requirements for CESAR1 can be up to 15% lower than 30% w/w MEA, probably ~10% lower than 35% w/w MEA, but in some runs no advantage was seen for CESAR1. The poorer examples of CESAR1 energy performance have been attributed (Hume, 2022) to solvent ‘damage’ after a period of operation (but after a much shorter period than would be encountered in commercial operation).

Comparison of MEA and CESAR1 on in-between issues

Process upsets triggering closure – could exceed annual emission allowances in short period. For both solvents problems in the water or acid washes could lead to much higher amine losses than normal. This highlights the need for both continuous emission monitoring and condition monitoring on key equipment.

Corrosion – reduced equipment lifetime or increased waste disposal costs – catalytic effect on degradation. Corrosion is expected to be a greater potential problem with MEA then CESAR1, but this is on the basis of tests where continuous reclaiming has not been used. MEA degradation products appear to enhance corrosion rates and corrosion products appear to enhance degradation rates. Thermal reclaiming on MEA has been shown, however, to give complete removal of both corrosion products and degradation products. So the expectation is, although yet to be verified by appropriate testing, that continuous thermal reclaiming at a high enough rate will maintain both corrosion and degradation of MEA at relatively low rates.

Solvent inventory or waste streams may be hazardous material. As already discussed, if the concentration of inherently-stable nitrosamines in CESAR1 cannot be continuously maintained at a low level then this introduces a particular hazard. For both solvents, given the range of chemical species, metals etc. that can be concentrated in reclaiming/cleaning residues, these are highly likely to be needed to be treated as hazardous materials unless extensive testing in actual commercial operation were to indicate otherwise.

Overall conclusions for subsequent techno-economic assessment

Based on the limited testing and publishing of results to date the main differences between MEA and CESAR1 for the purposes of the techno-economic assessment of post-combustion amine capture being undertaken in the next work package, as a baseline for comparison with the MCFC, appear to be:

a) At most, 15% lower specific reboiler duty (SRD) than MEA for CESAR1. This reduction will be used in sensitivity analyses.

b) Unproven differences in solvent management costs but those for CESAR1 expected to be somewhat higher, Weir (2023) suggests by a factor of two or more, than those for MEA. The approximate factor by which solvent management costs would have to increase to offset a reduced SRD will be estimated and compared with this factor of two.