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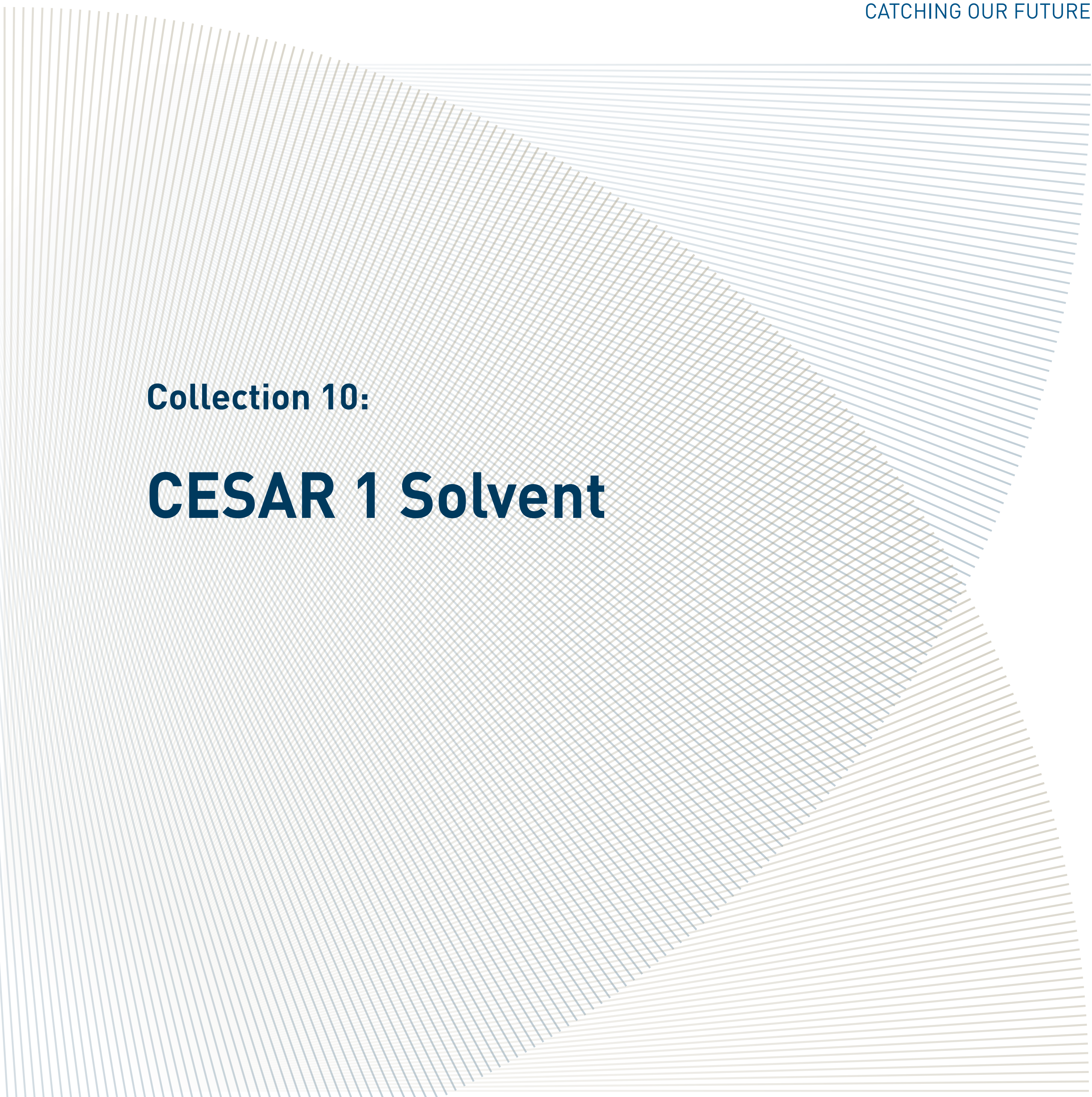

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Atmospheric emissions of amino-methyl-propanol, piperazine and their degradation products during the 2019–20 ALIGN-CCUS campaign at the Technology Centre Mongstad

(2021)

15th International Conference on Greenhouse Gas Control Technologies, GHGT-15

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Atmospheric emissions of amino-methyl-propanol, piperazine and their degradation products during the 2019-20 ALIGN-CCUS campaign at the Technology Centre Mongstad

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Abstract

In the frame of the 2019-20 ALIGN-CCUS campaign, the amine plant at the Technology Centre Mongstad (TCM) was operated with the CESAR 1 solvent, i.e. an aqueous solution of 2-amino-2-methylpropan-1-ol (AMP) and piperazine (PZ), for removing carbon dioxide from the flue gas of Equinor's combined cycle gas turbine plant. An online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) was used for quantifying atmospheric emissions of AMP and PZ, as well as emissions of amine degradation products and solvent impurities. Mean and median AMP levels emitted to the atmosphere over an operational period of 13 weeks were 562 and 377 ppb, respectively. PZ emissions to the atmosphere were much lower, with mean and median levels being 6.0 and 0.4 ppb, respectively. Three small carbonyl species (formaldehyde, acetaldehyde, acetone) were emitted at levels of tens to hundreds of ppb. Nitrogen-containing degradation products and impurities of solvent amines with mean emission levels >1 ppb included the following compounds: monomethylamine (MMA), formamide (FA), morpholine (MOR), 4,4-dimethyloxazolidine (DMO), 2-methyl-2-(methylamino)propan-1-ol (MeAMP), 4-acetylmorpholine (AMOR) and a compound with a molecular sum formula of $C_8H_{14}N_2$, which we tentatively assigned to an alkylated imidazole or pyrazole. Low (<5 ppm) emissions of AMP were associated with a low flue gas temperature (<38 °C) and large temperature gradient between the two water wash sections.

Keywords: Amines; 2-amino-2-methyl-1-propanol (AMP); Piperazine (PZ); PTR-MS; TCM; Carbon Capture

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1. Introduction

Amine-based post-combustion carbon capture (PCCC) is the technologically most mature solution for removing carbon dioxide (CO_2) from a flue gas stream. The reduction in CO_2 emissions comes, however, at the expense of amine emissions to the atmosphere. Atmospheric oxidation processes may partially transform the emitted amines into nitrosamines and nitramines [1], which are substances with known carcinogenic or potential carcinogenic properties. Since it is not possible to monitor and surveil nitrosamines and nitramines at ambient sub-ng/m³ levels, exposure to nitrosamines and nitramines is usually calculated taking into account dispersion and atmospheric processing of emitted amines. A key input parameter to such calculations is the emission rate of solvent amines and of smaller amines formed during solvent degradation. Amine emission data are thus of pivotal importance for ensuring an environmentally safe operation of an amine-based PCCC plant. A recent review by Scottish Environment Protection Agency [2] concludes that there is limited open source data available on amine emissions to the atmosphere and that most available data is based on capture solvents such as monoethanolamine (MEA) that are not necessarily representative of the mix of solvents used in state-of-the-art PCCC plants.

Nomenclature

ALIGN	Accelerating Low CarboN Industrial Growth
CCUS	Carbon Capture Utilization and Storage
TCM	Technology Centre Mongstad
PCCC	Post-combustion carbon capture
CCGT	Combined cycle gas turbine
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
WW	Water wash
CO_2	Carbon dioxide
AMP	2-amino-2-methyl-1-propanol
PZ	Piperazine
MEA	Monoethanolamine
MMA	Mmonomethylamine
FA	Formamide
MOR	Morpholine
DMO	4,4-dimethyloxazolidine
MeAMP	2-methyl-2-(methylamino)propan-1-ol
AMOR	4-acetylmorpholine

The Technology Centre Mongstad (TCM) (www.tcmda.com) in Norway is one of the world's leading facilities for testing and improving CO_2 capture technologies. TCM's tasks also include the assessment of amine emissions to the atmosphere and the development of emission reduction strategies. Only few results from the emission measurements have, however, hitherto been disclosed. This is because detailed emission data would reveal the chemical composition of the solvent, which is, in most cases, confidential business information. Therefore, only MEA emission data are currently available in the open literature [3, 4].

ALIGN-CCUS (Accelerating Low CarboN Industrial Growth through Carbon Capture Utilisation and Storage) is a project financed through the first ERA-NET Co-fund ACT program funded by nine European countries and the European Union Horizon 2020 program. The ALIGN consortium includes 31 partners from industry, research and academia and has considerable involvement of industrial companies and an enterprise organization. The ALIGN-CCUS project aims at accelerating the transition of current industry and power sectors into a future of continued economic activity and low-carbon emissions, in which carbon capture, utilization and storage (CCUS) plays an essential role. For optimizing and reducing costs of PCCC, the ALIGN consortium has implemented test programs at four different pilot plants and testing facilities including TCM, the SINTEF pilot rig at Tiller/Trondheim in Norway, RWE's Coal Innovation Centre at Niederaussem in Germany, and the Pilot-scale Advanced CO_2 Capture Technology

(PACT) facilities in Sheffield in the United Kingdom. TCM's contribution to the ALIGN-CCUS project is aimed at bridging knowledge gaps as well as reducing HSE, technical and financial risks of technology upscaling.

In the 2019-20 ALIGN-CCUS campaign at TCM, flue gas from Equinor's combined cycle gas turbine (CCGT) plant in Mongstad was treated with the aqueous 2-amino-2-methylpropan-1-ol (AMP) / piperazine (PZ) (CESAR 1) solvent. The CESAR 1 solvent was selected due to its lower energy consumption and higher stability as compared to MEA. Among the topics of the study were emission control and monitoring as well as solvent consumption. The main goal of the campaign was to demonstrate that this advanced amine solvent can be used at a large scale and with a real flue gas.

Results from the ALIGN-CCUS project are in the open domain, and we are herein reporting, for the first time, atmospheric emission data of AMP, PZ and their degradation products.

2. Method

The ALIGN-CCUS 2019-2020 campaign was carried out at TCM from September 12, 2019 to January 10, 2020. Flue gas from Equinor's CCGT plant in Mongstad was treated in TCM's amine plant operating with the CESAR 1 solvent. The chemical-analytical set-up to measure atmospheric emissions of amines, amine impurities and amine degradation products is described in detail in a companion paper [5]. Herein, we only use the data collected with an online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) [3]. The calibration of AMP and PZ is also described in the companion paper. Formaldehyde, acetaldehyde and acetone as well as acetonitrile were calibrated using a dynamically diluted calibration gas standard (Apel-Riemer Environmental, Inc., Miami, FL, U.S.A.). All other compounds are reported as acetone-equivalents, i.e. the acetone response factor was used for signal quantification. Reported volume mixing ratios have an accuracy of ±10% for calibrated compounds, and ±50% for compounds reported as acetone-equivalents.

3. Results and discussion

3.1. Atmospheric emissions of AMP and PZ

Figure 1 shows the distribution of AMP and PZ volume mixing ratios, respectively, as measured during the 2019-2020 ALIGN-CCUS campaign at TCM. Mean and median AMP levels emitted were 562 and 377 ppb, respectively. PZ emissions were much lower, with mean and median levels being 6.0 and 0.4 ppb, respectively. The mean value is significantly higher than the median value because of sporadic PZ bursts. No experimental data are available in the open literature to compare our data with. Kolderup et al. [6] carried out modeling simulations and estimated total AMP and PZ emissions in the 0.55 – 30 ppm range. The AMP levels observed in this study were similar to MEA levels found in previous work at TCM [7, 4, 8]. Notably, AMP emissions were typically three orders of magnitude higher than PZ emissions. Khakharia et al. [9] reported an AMP-to-PZ emission ratio of 26, while Mertens et al. [10] found two orders of magnitude higher AMP emissions as compared to PZ. This discrepancy cannot be explained by the AMP-to-PZ-ratio in the solvents (3 M AMP and 1.8 M PZ in the Mertens et al. study [10]; 3.6 M AMP and 0.9 M PZ in the Khakharia et al. study [9]; 3 M kg^{-1} AMP and 1.5 M kg^{-1} PZ in the CESAR 1 solvent). The low PZ emission levels observed during the ALIGN-CCUS campaign can be explained by a low entrainment rate of PZ into the gas phase and/or more efficient scrubbing of PZ in the water wash sections.

3.2. Atmospheric emissions of amine degradation products and impurities

10 amine degradation products and 1 solvent impurity were emitted to the atmosphere with a mean and median volume mixing ratio above 1 ppb during the ALIGN-CCUS 2019-2020 campaign (Figure 2). Three small carbonyl species (formaldehyde, acetaldehyde, acetone) were emitted at levels of tens to hundreds of ppb, with acetone reaching the highest levels. It was observed previously [12, 13] that acetone is a major decomposition product of an aqueous AMP/PZ blend. Seven of the remaining species that were emitted to the atmosphere included one nitrogen atom: monomethylamine (MMA), formamide (FA), morpholine (MOR), 4,4-dimethyloxazolidine (DMO), 2-methyl-2-(methylamino)propan-1-ol (MeAMP), and 4-acetylmorpholine (AMOR). The remaining compound has a molecular

sum formula of $C_8H_{14}N_2$, which we tentatively assign to an alkylated imidazole or pyrazole. Notably, MMA was emitted at a mean level of almost 20 ppb. Wang [12] expected MMA to be formed from AMP degradation but did not detect it. Wang [12] also observed the formation of formamide when exposing AMP to UV radiation. MeAMP is a common impurity of AMP and DMO has been observed as a decomposition compound in the liquid phase [12]. But so far, they have not been reported as being released to the atmosphere. MOR, AMOR and $C_8H_{14}N_2$ have not been reported previously. It is also noteworthy that 1-nitrosopiperazine was detected in the emitted flue gas. A tentative quantification puts emission levels well below 1 ppb, but more calibration work is needed for quantifying nitrosamines.

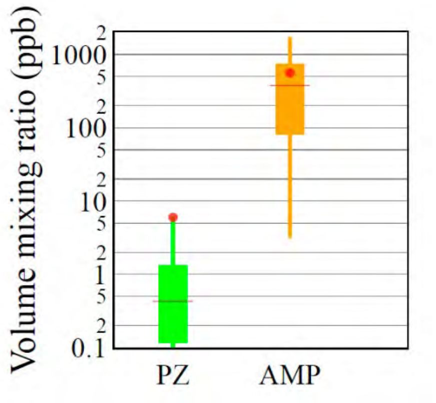

Fig. 1. Distribution of volume mixing ratios of PZ and AMP emitted to the atmosphere when flue gas from Equinor's CCGT plant in Mongstad was scrubbed of CO_2 in TCM's amine plant operating with the CESAR 1 solvent. Boxes represent 25th and 75th percentiles, the horizontal line is the median, the dot is the mean, and whiskers represent 5th and 95th percentiles.

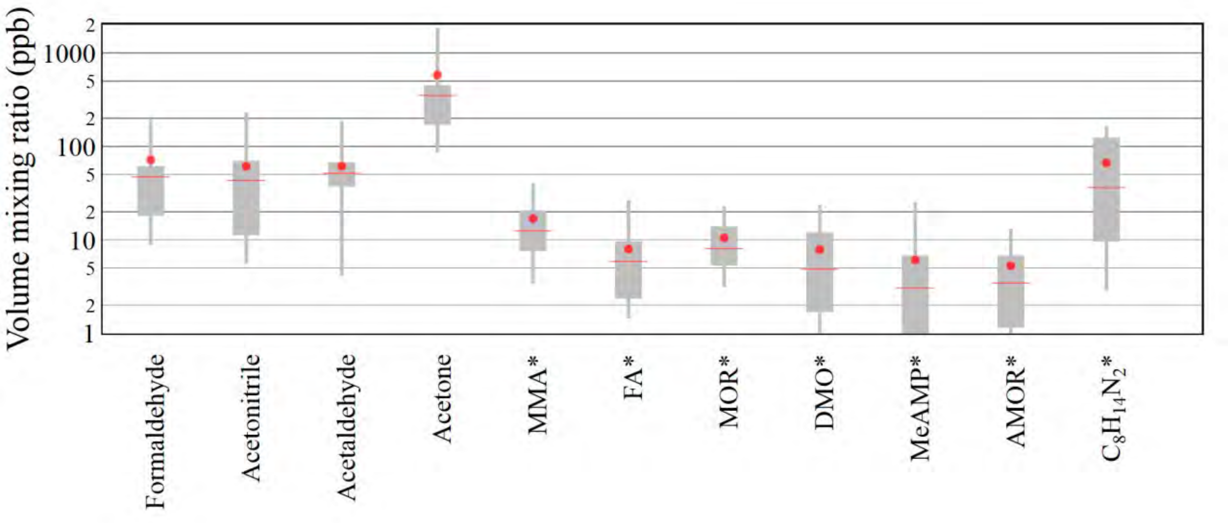

Fig. 2. Distribution of the 10 amine degradation products and 1 solvent impurity (MeAMP) that were emitted to the atmosphere with a mean level > 1 ppb. Boxes represent 25th and 75th percentiles, the horizontal line is the median, the dot is the mean, and whiskers represent 5th and 95th percentiles. Compounds marked with an asterisk (*) are reported as in acetone-equivalent mixing ratios (see text).

3.3. Impact of the operational parameters of the plant

The operating parameters of the amine plant obviously influence the level of emissions. Mertens et al. [10] found that emissions depend upon the flue gas temperature and the temperature gradient over the water wash (WW) section. Our initial analysis thus focused on the effect of these two parameters on atmospheric emissions. Figure 3 (upper panel) shows that high (>5 ppm) AMP emissions were associated with high (>38 °C) flue gas temperatures. Figure 3 (lower panel) on the other hand shows that high AMP emissions only occurred when the temperature gradient between the two WW sections was low. Emissions of PZ and degradation products exhibited similar trends. More details will be disclosed in a forthcoming paper.

Our findings are thus in agreement with the observations by Mertens et al. [10], and this information may be used to mitigate emissions from amine plants. Previous work [9, 11] has, however, also shown that other parameters such as solvent temperature, pH and CO_2 content significantly impact atmospheric emissions. The effect of additional parameters will be investigated in future work.

Finally, we would like to point out that the results shown here were obtained when the amine plant was operated with flue gas from the CCGT plant. This flue gas has a low acidic content, which prevents the formation of aerosol particles ("mist") in the absorber column. Currently ongoing studies indicate that emission profile changes significantly when the amine plant runs on the other flue gas available at TCM, which is from the Residue Fluid Catalytic Cracker (RFCC). The results from these ongoing studies will be presented in future work.

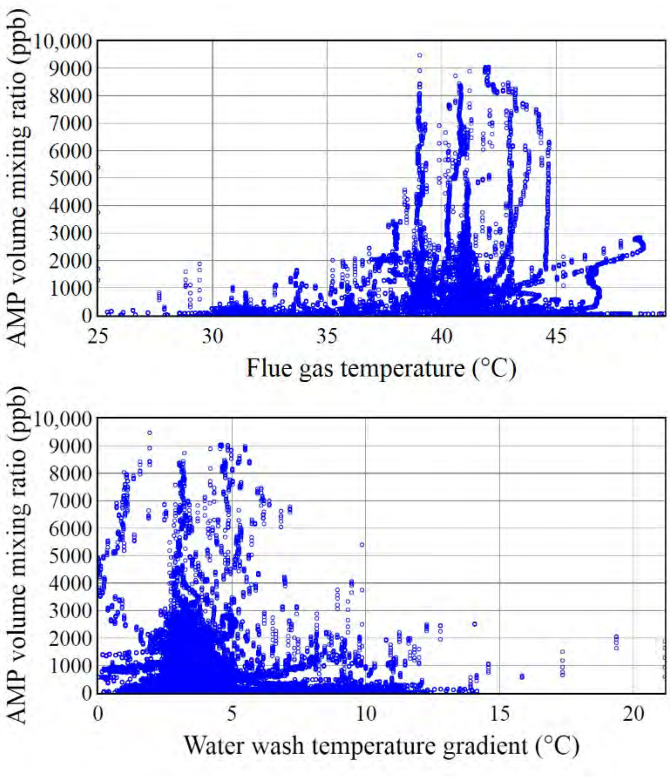

Fig. 3. Scatter plots of AMP emissions versus flue gas temperature (upper panel) and AMP emissions versus the temperature gradient over the water wash sections (lower panel). Data associated with flue gas temperatures below 25 °C were not included in the analysis. Such low temperatures only occur during the plant warm-up and not during regular plant operation.

Conclusions

We herein report, for the first time, the levels of AMP and PZ as well as of their degradation products that are emitted into the atmosphere from a PCCC plant, which was operated on the CESAR 1 solvent. Significant emissions of AMP and of two small reactive carbonyls (formaldehyde, acetaldehyde) will need to be considered in any atmospheric impact assessment study, while minor emissions of other degradation products (in particular of 1-nitrosopiperazine) warrant further investigations. We also characterized the impact of specific plant parameters on emissions and found that high (>5 ppm) AMP emissions were associated with a high flue gas temperature (>38 °C) and small temperature gradient between the two water wash sections. A more in-depth analysis of the collected data will allow us to give recommendations for mitigating emissions from amine-based PCCC plants operating on the advanced CESAR 1 solvent.

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Best practices for the measurement of 2-amino-2-methyl-1-propanol, piperazine and their degradation products in amine plant emissions

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Best practices for the measurement of 2-amino-2-methyl-1-propanol, piperazine and their degradation products in amine plant emissions

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Abstract

We herein present the chemical-analytical setup used to measure atmospheric emissions of amines and amine degradation products from an amine-based post-combustion carbon capture plant. The emission measurements were carried out at the Technology Centre Mongstad (TCM) in Norway, in the frame of the ALIGN-CCUS campaign from September 2019 to January 2020, when the amine plant was operated with the CESAR 1 solvent. This advanced solvent is an aqueous solution of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ). Four chemical-analytical techniques were deployed for characterizing emission of AMP, PZ and their degradation products: online Fourier Transform Infrared (FTIR) Spectroscopy, online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS), online Proton-Transfer-Reaction Quadrupole Mass Spectrometry (PTR-QMS), as well as manual impinger sampling followed by offline Ion Chromatography Mass Spectrometry (IC-MS) analysis. AMP was detected by all four methods, with the results being in reasonably good agreement. PZ was detected by PTR-TOF-MS, PTR-QMS and IC-MS, but because of the low emission levels (single-digit ppb) the latter two methods suffered from a positive bias (due to an interfering compound) and a large measurement uncertainty, respectively. 17 amine degradation products were only detected by the PTR-ToF-MS analyzer. We present exemplary results from the emission measurements carried out during the ALIGN-CCUS 2019-2020 campaign and share some of the lessons learned from this exercise.

Keywords: amines; 2-amino-2-methyl-1-propanol (AMP); piperazine (PZ); PTR-MS; TCM.

Introduction

Amine-based post-combustion carbon capture (PCCC) is the technologically most mature solution for removing carbon dioxide (CO_2) from a flue gas stream. The reduction in CO_2 emissions does, however, come at the expense of amine emissions to the atmosphere [1]. Atmospheric oxidation processes may partially transform the emitted amines

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into nitrosamines and nitramines [2], which are substances with known carcinogenic or potential carcinogenic properties. Based on a conservative risk analysis, inhalation exposure to the sum of PCCC-derived nitrosamines and nitramines should be kept below an annual average concentration of only 0.3 ng m^{-3} [3] for the general public. Since it is not possible to monitor such low concentrations in the atmosphere, exposure to nitrosamines and nitramines is calculated taking into account emission rates of amines, as well as the dispersion and atmospheric processing of emitted amines. Amine emission rates need to be measured, but their low concentrations (typically 0.1-10 ppm) and the high humidity levels in the treated flue gas make this a challenging analytical effort.

Nomenclature

ALIGN	Accelerating Low CarboN Industrial Growth
CCUS	Carbon Capture Utilization and Storage
TCM	Technology Centre Mongstad
PCCC	Post-combustion carbon capture
CCGT	Combined cycle gas turbine
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
PTR-QMS	Proton-Transfer-Reaction Quadrupole Mass Spectrometry
FTIR	Fourier Transform Infrared
IC-MS	Ion Chromatography Mass Spectrometry
VP	Vaporizer
HF	Heated filter
PCR	Principal component regression
SS	Stainless steel
PTFE	Polytetrafluoroethylene
CO_2	Carbon dioxide
AMP	2-amino-2-methyl-1-propanol
PZ	Piperazine
MEA	Monoethanolamine

The Technology Centre Mongstad (TCM) (www.tcmda.com) in Norway is one of the world's leading facilities for testing and improving CO_2 capture technologies. TCM's tasks also include the validation and optimization of emission sampling and measurement techniques. TCM has put considerable efforts into the characterization of atmospheric emissions and nowadays routinely monitors amines in the absorber effluent stream using a variety of analytical methods [4]. These include online Fourier Transform Infrared (FTIR) Spectroscopy, online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) [5], online Proton-Transfer-Reaction Quadrupole Mass Spectrometry (PTR-QMS) [6], as well as manual impinger sampling followed by offline Ion Chromatography Mass Spectrometry (IC-MS) analysis [4]. While amine emission data are routinely reported to the authorities, only few results have hitherto been publicly disclosed because the solvent composition is, in most cases, confidential.

ALIGN-CCUS (Accelerating Low CarboN Industrial Growth through Carbon Capture Utilisation and Storage) is a project financed through the first ERA-NET Co-fund ACT program funded by nine European countries and the European Union Horizon 2020 program. The ALIGN consortium includes 31 partners from industry, research and academia and has considerable involvement of industrial companies and an enterprise organization. The ALIGN-CCUS project aims at accelerating the transition of current industry and power sectors into a future of continued economic activity and low-carbon emissions, in which carbon capture, utilization and storage (CCUS) plays an essential role. For optimizing and reducing costs of PCCC, the ALIGN consortium has implemented test programs at four different pilot plants and testing facilities including TCM, the SINTEF pilot rig at Tiller/Trondheim in Norway, RWE's Coal Innovation Centre at Niederaussem in Germany, and the Pilot-scale Advanced CO_2 Capture Technology (PACT) facilities in Sheffield in the United Kingdom. TCM's contribution to the ALIGN-CCUS project is aimed at bridging knowledge gaps as well as reducing HSE, technical and financial risks of technology upscaling.

In the ALIGN-CCUS 2019-2020 campaign at TCM, flue gas from Equinor's combined cycle gas turbine (CCGT) plant in Mongstad was treated with the aqueous 2-amino-2-methyl-1-propanol (AMP) / piperazine (PZ) (CESAR 1) aqueous solvent. The CESAR 1 solvent was selected due to its lower energy consumption and higher stability as compared to monoethanolamine (MEA). Its promising characteristics have made CESAR 1 the new benchmark IEAGHG amine solvent. Emission control and monitoring as well as solvent consumption were among the study topics of the ALIGN-CCUS 2019-2020 campaign. The main goal of the campaign was to demonstrate that this advanced amine solvent can be used at a large scale and with a real flue gas. Results from the ALIGN-CCUS project are in the open domain, thus offering the opportunity to show, for the first time, qualitative and quantitative results on the measurement of AMP and PZ in the absorber effluent. Emission data will be presented in a companion paper.

In this work, we will present the chemical-analytical methods used for carrying out the emission measurements during the ALIGN-CCUS 2019-2020 campaign and present some of the results along with the lessons learned from this exercise.

Methods

2.1. Overview of the campaign and overall system description

The ALIGN-CCUS campaign at TCM was conducted from September 12th 2019 to January 10th 2020. As already stated above, flue gas from a CCGT plant was treated with the CESAR 1 solvent. Figure 1 is a sketch of the analytical set-up used for emission monitoring. Table 1 gives an overview of the analytical methods used for emission monitoring, their time of deployment, the measurement frequency and the compounds measured.

Table 1. Overview of the analytical methods used for emission monitoring, their time of deployment, the measurement frequency and the compounds measured.

Type	Instrument	Start	End	Time step	Compounds measured
Online	PTR-TOF-MS	12-09-2019	10-01-2020	1 min	AMP, PZ + 17 degradation products
	PTR-QMS	12-09-2019	10-01-2020	1 min	AMP (+PZ, positive bias due to interfering compound)
	FTIR	12-09-2019	10-01-2019	5 min	AMP
Offline	Impinger/IC-MS	13-09-2019	19-12-2019	12 samples	AMP (+ PZ, not quantified due to high uncertainty)

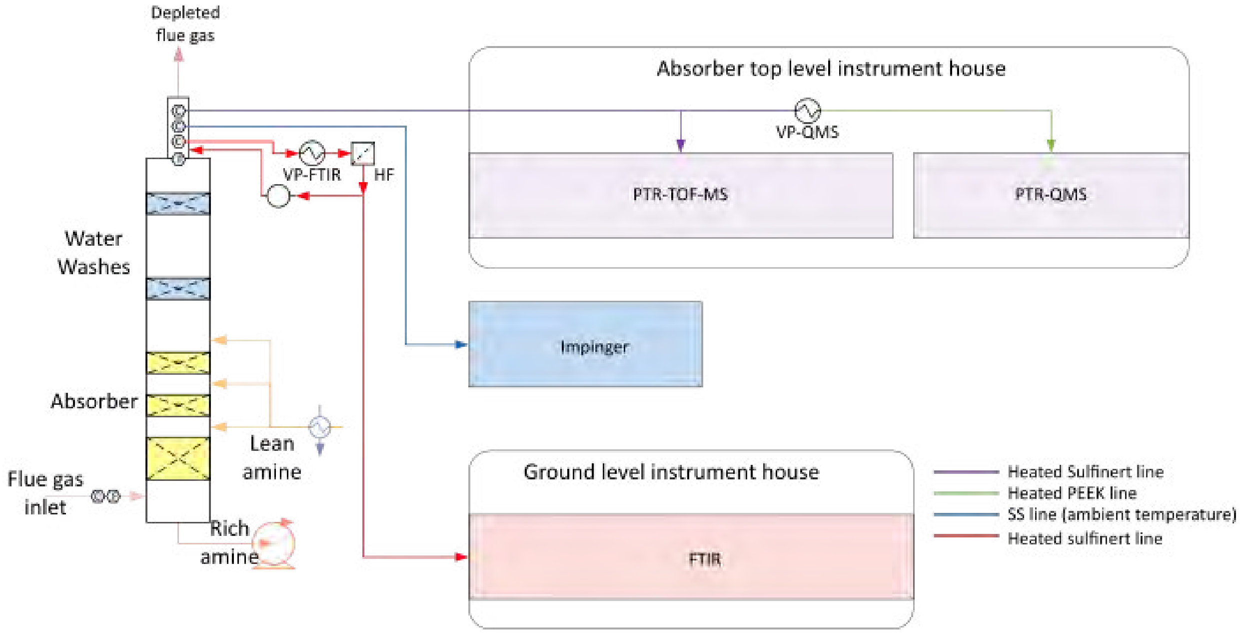

Fig. 1. Process flow diagram of emission sampling of absorber outlet. (VP: vaporizer)

2.2. Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

PTR-MS is a well-established technique for monitoring organic trace gases online (*i.e.*, without sample pre-treatment), at a typical measurement frequency of 1 Hz and down to ppt levels [7]. In PTR-MS, the gas to be analyzed is introduced into a low-pressure reaction cell wherein organic molecules are softly ionized via gas-phase proton transfer reactions with H_3O^+ ions [8]. The protonated analyte molecules are detected in a quadrupole mass spectrometer (QMS) or a time-of-flight mass spectrometer (TOF-MS). [5] have described the use of PTR-MS for monitoring amines in the treated flue gas emanating from an amine-based PCCC plant. For the work presented herein, we used two different PTR-MS instruments, a PTR-TOF-MS analyzer (model PTR-TOF 8000; Ionicon Analytik, Innsbruck, Austria) and a PTR-QMS instrument (model QMS 300; Ionicon Analytik, Innsbruck, Austria). The latter is a cheaper and easier to use instrument version, which was conceived for industrial monitoring purposes. Both instruments were placed in an analyzer house on top of the absorption tower, and connected to the stack via a ~10 m long heated (120 °C) sampling line made of SilcoNert2000®/Sulfinert. The subsampling line of the PTR-QMS instrument included a vaporizer (VP-QMS) for evaporating potential mist particles. The operating parameters of both PTR-MS instruments were as follow: drift tube pressure 2 mbar, drift tube temperature 120 °C, drift tube voltage 500 V. The resulting reduced electric field strength (E/N) was ~150 Td (1 Td = 10^{-17} V.cm^2).

Both PTR-MS instruments were calibrated for AMP and PZ using a HovaCAL® calibration gas generator (model 312-MF; IAS GmbH, Oberursel, Germany). A quantitative aqueous amine solution (AMP, PZ) was prepared by TCM's analytical laboratory. This solution was evaporated at 180 °C in the HovaPOR evaporator (IAS GmbH, Oberursel, Germany) under a pure nitrogen atmosphere. By increasing the calibration solution flow into the evaporator, the humidity increases in the resulting calibration gas. This allowed us to study the response of the two PTR-MS instruments at different humidity levels.

2.3. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR instrument (Analect 5000; Schneider Electric) was located in the analyzer house at the bottom of the absorption tower. It was connected to the stack via a 100 m long sampling line made of SilcoNert2000®/Sulfinert. The flue gas was extracted from the stack at a fixed flow rate using a fast flow loop system mimicking isokinetic conditions [9]. The fast flow loop system included a vaporizer (VP-FTIR) for evaporating potential mist particles and a heated filter (HF). The temperatures of these units were adjusted to minimize the thermal degradation of analytes. The FTIR instrument was calibrated using the same HovaCAL® calibration gas generator as described above. Principal component regression (PCR) models were used for extracting CO_2, H_2O, NO, NO_2, SO_2, NH_3, acetaldehyde, formaldehyde, AMP and PZ from the FTIR spectra.

2.4. Impinger sampling followed by Ion Chromatography Mass Spectrometry (IC-MS) analysis

Samples were extracted isokinetically and collected in a standard impinger sampling train including a condensation flask, a filter flask and three absorption flasks. Typical sampling times were 1-2 hours. The samples were analyzed in TCM's laboratory using a Dionex Integrion HPIC System (model ICS-5000, Thermo Fisher Scientific) which included an IonPac CS19 column and an IonPac CG19 guard column.

Results and Discussion

3.1. Measurement of AMP emissions and encountered difficulties

The only compound detected by all four measurement techniques was AMP. The results obtained with the four methods were in good agreement. As shown in Figure 2, the distribution of the measured AMP volume mixing ratios was very similar, with the PTR-TOF-MS, the PTR-QMS and the FTIR instrument measuring median AMP levels of 433, 400 and 388 ppb, respectively. Mean measured AMP levels were 592, 549 and 503 ppb, respectively. Figure 3 shows an exemplary time series of AMP as recorded over a period of ten days. Two impinger samples were collected during this period. The measurements are again in good agreement, the only major discrepancy being the systematically lower levels measured by the FTIR instrument during periods with enhanced emissions. Table 2 shows a systematic comparison for all data collected during twelve impinger sampling periods, with sample collection times ranging from 42 to 136 minutes. The overall agreement was good, even though in some case large discrepancies were observed. It is not clear why the level of agreement varied between the samples. Future work is needed for addressing this issue.

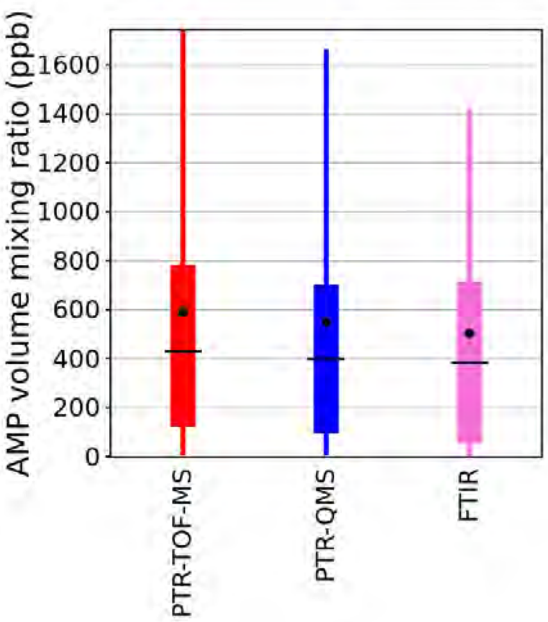

Fig. 2. Distribution of AMP volume mixing ratios as measured in the emitted flue gas by the PTR-TOF-MS, PTR-QMS and FTIR instruments, respectively, over the duration of the whole 2019-2020 ALIGN-CCUS campaign. Boxes represent 25th and 75th percentiles, the black line is the median, and the black dot is the mean. Whiskers represent 5th and 95th percentiles.

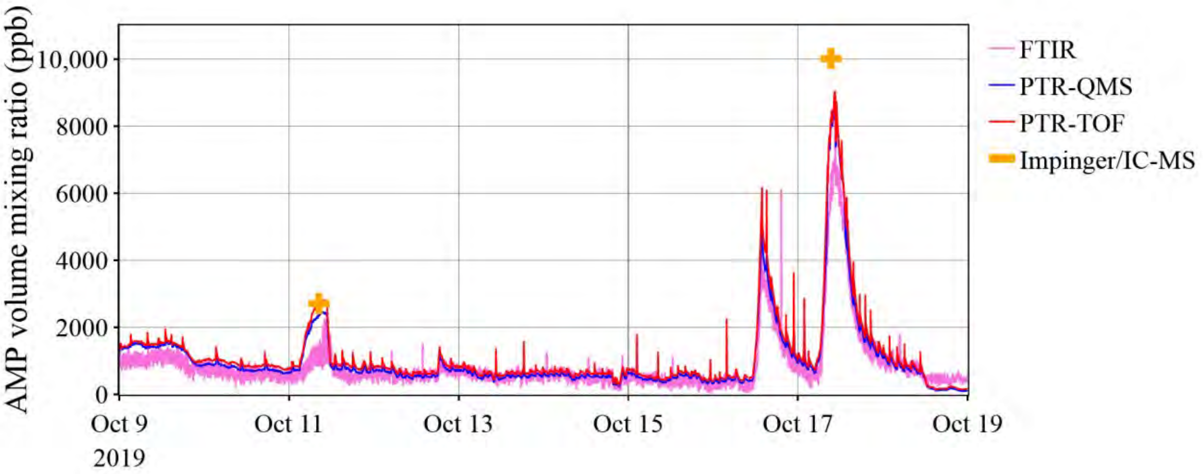

Fig. 3. Exemplary time series of AMP volume mixing ratios as measured in the emitted flue gas by the PTR-TOF-MS, PTR-QMS and FTIR instruments, respectively, in the period from October 9 to October 19, 2019. Also included are the two discrete measurement points obtained via impinger sampling followed by IC-MS analysis.

Table 2. AMP mixing ratios as measured by all four measurement techniques during the impinger sampling periods. Standard deviations are given in brackets.

		AMP (ppb)			
Date	Sampling time (min)	PTR-TOF-MS	PTR-QMS	FTIR	Impinger/IC-MS
2019-09-13	120	470 (33)	416 (26)	18 (21)	740
2019-09-18	60	1009 (25)	1043 (41)	0 (0)	1270
2019-09-24	60	1449 (28)	1271 (12)	521 (131)	1660
2019-09-26	72	1073 (93)	1049 (50)	1042 (107)	1140
2019-10-01	60	1892 (27)	1814 (30)	1393 (150)	2680
2019-10-11	114	2708 (73)	2356 (63)	1209 (263)	2710
2019-10-17	60	8027 (280)	7939 (286)	6113 (452)	10010
2019-10-22	137	495 (37)	461 (37)	103 (55)	950
2019-10-29	128	37 (1)	39 (8)	258 (69)	588
2019-12-11	136	447 (15)	339 (16)	150 (112)	831
2019-12-19	68	30 (3)	12 (1)	14 (19)	110
2019-12-19	42	3893 (462)	3242 (359)	2423 (512)	9200

A number of problems and difficulties were observed for all of the measurement methods used during the ALIGN-CCUS campaign. A forthcoming paper will address these issues in more detail and only a brief outline is given here.

The FTIR analyzer was sampling through a 100 m long sampling line. Long sampling lines are known to require long conditioning times for amines, meaning that peak levels were dampened and thus underestimated. In addition, we found that a stainless steel (SS) line originally connected to the FTIR instrument was corroded. The SS line was replaced with a sampling line made of polytetrafluoroethylene (PTFE) during the campaign. AMP degrades when in contact with a hot SS surface. It was thus important to reduce the temperature of the vaporizer (see Figure 1) to a level at which no AMP decomposition is observed. Finally, it should be noted that the AMP concentrations in the treated flue gas were close to the detection limit of the FTIR instrument, which made the measurements with this instrument less accurate.

The response of PTR-MS instrument to amines usually does not depend on the humidity of the sample matrix. This was not the case for AMP. The response of the PTR-QMS and the PTR-TOF-MS instruments varied by a factor of 5 between dry and humid conditions. For obtaining accurate results, it was essential to calibrate both instruments over the full range of humidity levels observed in the flue gas stack. Also, the reduction, processing and analysis of the PTR-TOF-MS data was highly complex and time-consuming and required a full time engagement of an expert scientist.

Impinger sampling followed by ICMS analysis is time consuming and laborious. Only 12 samples were thus collected and analysed over a period of the whole campaign. In addition, the measurement uncertainty was high at low ppb levels. Only AMP (typically >100 ppb) was thus quantitatively reported from the IC-MS analysis.

Finally, it should be noted, that during the ALIGN-CCUS campaign no mist was observed in the treated flue gas. Measurement problems that occurred in the presence of mist will be presented in a separate study.

3.2. Measurement of PZ

PZ was only present at low ppb levels in the treated flue gas, meaning that only the PTR-TOF-MS instrument was able to quantitatively detect it. PZ also exhibited a humidity-dependent response. It was thus necessary to carry out a humidity-dependent calibration of the PTR-TOF-MS instrument. The PTR-QMS instrument also detected an ion signal at *m/z* 87, which corresponds to protonated PZ. An intercomparison with the PTR-TOF-MS data revealed that a second peak at *m/z* 87 (which can only be resolved by the PTR-TOF-MS and not by the PTR-QMS) becomes quantitatively relevant at low ppb levels. Since these were typical emission levels during the ALIGN-CCUS 2019-2020 campaign at TCM, it was not possible to quantitatively measure PZ with the PTR-QMS instrument. Impinger sampling followed by offline Ion Chromatography Mass Spectrometry (IC-MS) analysis suffered from a high measurement uncertainty at low ppb levels, meaning that not quantitative PZ data were reported during the ALIGN-CCUS 2019-2020 campaign.

3.3. Measurement of solvent degradation products

The PTR-TOF-MS analyzer also detected a series of solvent degradation products. The high mass accuracy (typically <10 ppm) of the measurement combined with an isotopic pattern analysis allowed us to identify the elemental composition (i.e., the molecular sum formula) of the decomposition products. Table 3 lists the *m/z* of the main signals detected in the flue gas, the assigned molecular sum formula and the name of the compound that we assigned (or tentatively assigned) to this signal based on previous work specified in the fourth column. An identification of compounds with a higher degree of confidence warrants complementary analyses by GC-MS or LC-MS.

Table 3. Main *m/z* signals detected by the PTR-TOF-MS instrument in the flue gas that was emitted to the atmosphere when the amine plant was operated with the CESAR 1 solvent. The molecular sum formula was assigned unambiguously; the assignment to a specific chemical substance was based on chemical plausibility and literature data specified in the "References" column. Assignments marked with an asterisk are tentative.

m/z	**Molecular sum formula**	**Assignments**	**References**
87.092	$C_4H_{10}N_2$	Piperazine	
90.092	$C_4H_{11}NO$	2-Amino-2-methyl-1-propanol	
31.021	CH_2O	Formaldehyde	[10]
42.034	C_2H_3N	Acetonitrile	-
45.033	C_2H_4O	Acetaldehyde	[11]
59.049	C_3H_6O	Acetone	[10]
32.050	CH_5N	Methylamine	[11]
46.029	CH_3NO	Formamide	[10]
88.077	C_4H_9NO	Morpholine*	[4]
101.171	$C_2H_8N_2O$	2-Oxopiperazine	[10]
101.108	$C_5H_{12}N_2$	Methylpiperazine	[10]
102.092	$C_5H_{11}NO$	4,4-Dimethyloxazolidine	[10]
104.107	$C_5H_{13}NO$	2-Methyl-2-(methylamino)propan-1-ol*	-
115.088	$C_5H_{10}N_2O$	1-Formylpiperazine	[10]
116.071	$C_5H_9NO_2$	4,4-Dimethyl-1,3-oxazolidine-2-one	[10]
116.082	$C_4H_9N_3O$	1-Nitrosopiperazine	[10]
129.102	$C_6H_{12}N_2O$	1-Acetylpiperazine*	-
130.086	$C_6H_{11}NO_2$	4-Acetylmorpholine*	-
139.122	$C_8H_{14}N_2$	Alkylated imidazole* or pyrazole*	-

Conclusions

Amine-based PCCC plants emit a variety of organic chemicals into the atmosphere. Treatment of CCGT flue gas with the CESAR 1 solvent generates ppb-to-ppm levels of AMP in the emission stream. Our study has shown that such emissions can be measured with sophisticated chemical-analytical techniques (PTR-TOF-MS; impinger sampling/IC-MS) but also with less demanding methods that are suitable for routine industrial monitoring purposes (PTR-QMS, FT-IR). Special care must be taken to avoid losses (due to adsorption and/or thermal decomposition of AMP) in the inlet system and to calibrate the online analyzers. Only the PTR-ToF-MS instrument was capable of detecting PZ at low ppb levels, which were typical emission levels during the ALIGN-CCUS campaign. The PTR-TOF-MS analyser is also capable of detecting amine degradation products, 17 of which were observed at significant levels in the flue gas after treatment with the CESAR 1 solvent. The unambiguous identification of these degradation products would, however, require complementary analyses using highly specific offline GC/LC-MS^n methods.

While it seems unfeasible to make similar chemical-analytical efforts for emission characterization at each amine-based PCCC plant, TCM and its partners provide the know-how and infrastructure to characterize the emission profile of new solvents.

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CATCHING OUR FUTURE

First Process Results and Operational Experience with CESAR1 Solvent at TCM with High Capture Rates (ALIGN-CCUS Project)

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First Process Results and Operational Experience with CESAR1 Solvent at TCM with High Capture Rates (ALIGN-CCUS Project)

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Abstract

In 2019, the Technology Centre Mongstad (TCM) operated, in the frame of ALIGN-CCUS project, a test campaign using CESAR1 solvent, a blend of AMP and PZ. The main objective was to demonstrate CESAR1 operability and performance at large scale and produce knowledge that can be used to enhance the deployment of post-combustion capture at commercial scale. Tests were carried out on CCGT flue gas and varying process conditions and plant configurations. The current paper presents an overview of the test campaign and reports on energy performance, solvent consumption and operational experience. The CESAR1 solvent was found to require less energy than 30 wt% MEA considered as the reference. Although PZ degrades easily in presence of NO_2, the solvent consumption was kept low over the campaign. Solvent precipitation in the absorber was experienced in severe conditions. Successful mitigating actions were applied to reverse it and operating procedures were developed to avoid it.

Keywords: PCC; post-combustion capture; CO_2 capture; TCM

1. Introduction

The Technology Centre Mongstad (TCM) is the world's leading facility for verifying and improving CO_2 capture technologies. TCM is located at Mongstad, one of Norway's most complex industrial facilities, next to the Mongstad refinery operated by Equinor. TCM has been operating since autumn 2012, providing an arena for qualification of CO_2 capture technologies on an industrial scale. TCM is owned by Gassnova (on behalf of the Norwegian state), Equinor (formerly Statoil), Shell and Total. In 2019, TCM executed a test campaign with a non-proprietary solvent called CESAR1 in the frame of the ALIGN-CCUS project.

ALIGN-CCUS (Accelerating Low CarboN Industrial Growth through Carbon Capture Utilisation and Storage) is a project from the first ERA-NET Co-fund ACT program. In this program nine European countries, together with the

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European Union Horizon 2020 program are joining forces for research and actions. The ALIGN consortium involves 31 partners from industry, research and academia and has considerable involvement of industrial companies and an enterprise organization. The ALIGN-CCUS (ALIGN) project aims to accelerate the transition of current industry and power sectors into a future of continued economic activity and low-carbon emissions, in which carbon capture, utilization and storage (CCUS) plays an essential role. For the optimization and cost reduction of post-combustion capture (PCC) technology, the consortium realizes testing programs at four different pilot plants and testing facilities: the Technology Centre Mongstad (NOR), the SINTEF pilot rig at Tiller, Trondheim (NOR), RWE's Coal Innovation Centre at Niederaussem (DE) and the PACT facilities at Sheffield (UK). Collaboration of TCM with ALIGN-CCUS project is significant in bridging the knowledge gaps, and reducing HSE, technical and financial risks of technology deployment at large scale.

The test campaign has been carried out from September 2019 to January 2020 with a blend of aqueous 2-Amino-2-methylpropan-1-ol (AMP) and Piperazine (PZ). The amine concentrations were respectively 27 wt% and 13 wt%. This blend is called CESAR1 and has been developed during a former EU project (CESAR). This non-proprietary solvent is known to perform better than generic aqueous 30 wt% MEA and has been proposed by IEAGHG as their new benchmark [1]. It has potentially lower thermal energy consumption and lower solvent degradation rates than generic MEA. On the downside, AMP is volatile and may lead to relatively high emissions. In addition, PZ is a toxic compound and can also lead to precipitation at both very high and low CO_2 loading, in combination with other process parameters like temperature of the solvent and flus gas. The purpose of the test campaign was to develop knowledge related to emissions, degradation and safe operation in industrial environment with the CESAR1 solvent.

This paper describes in the first part the parametric testing performed in different configurations of the amine plant. Optimum performances were determined by varying the liquid to gas ratio at capture rates from 85% up to 98%. This high capture rate was selected as high capture rate, close to 100%, are expected in the near future. The absorber was operated with 12, 18 or 24m of packing. For this work, the TCM amine plant was operated with flue gas from the Equinor's CCGT plant at Mongstad. The second part describes TCM operational experience with the CESAR1 solvent.

Nomenclature

AMP	2-Amino-2-methylpropan-1-ol	ppmv	Parts per million by volume
Capex	Capital expenditure	PZ	Piperazine
CCGT	Combined Cycle Gas Turbine	RFCC	Refinery Fluid Catalytic Cracking
CHP	Combined Heat and Power	SCR	Selective Catalytic Reduction of NOx
DCC	Direct Contact Cooler	Sm^3/h	Standard conditions: 101.325 kPa and 15°C
HSE	Health, Safety and Environment	SRD	Specific Reboiler Duty
MEA	Monoethanolamine	TCM	Technology Centre Mongstad
Opex	Operational expenditure	wt%	weight percent

2. Initial assessment of CESAR1 performance at TCM

2.1. TCM amine plant

The amine plant is a generic and highly flexible CO_2 capture plant designed and constructed by Aker Solutions and Kværner. The amine plant captures CO_2 either from CCGT flue gas with a design CO_2 production capacity of 80 tonnes/day or from RFCC flue gas with a capacity of 200 tonnes/say. The ALIGN-CCUS campaign has been performed with CCGT flue gas. The plant was lined up with the CHP DCC and CHP stripper. Figure 1 given below shows a simplified process flow diagram of TCM amine plant. Flue gas from the blower is conditioned and saturated with water to the required temperature (normally 20-50°C) in the DCC. The lean amine solvent can be fed either at 12m, 18m or 24m to the absorber structured packed bed (highlighted in yellow in Figure 1). Rich amine from the absorber is pumped through the rich/lean cross plate heat exchanger to the top of CHP stripper. A slip stream of the cold rich amine is bypassed upstream the heat exchanger to the stripper overhead. A more detailed description of the amine plant is available elsewhere [2,3]

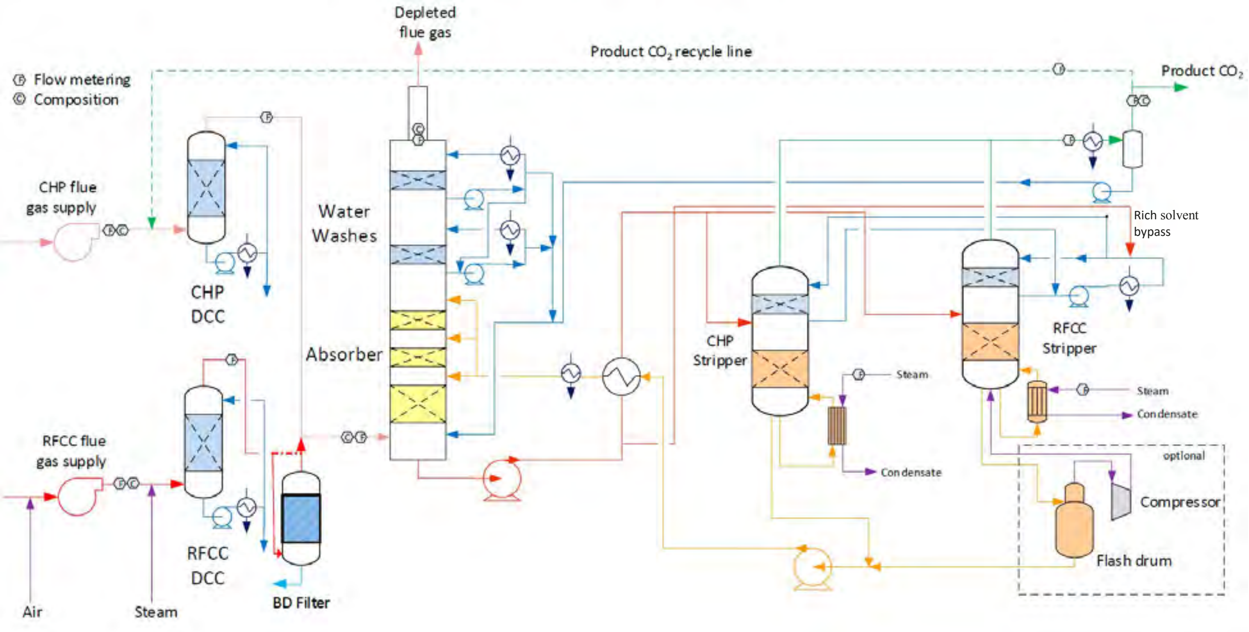

Figure 1. TCM Amine plant flowsheet

2.2. Test plan description

The test campaign started on September 12th, 2019. The storage tank was filled with 26 tonnes of a concentrated aqueous mixture of AMP (48.0 wt%) and PZ (23.7 wt%) supplied by Brenntag. The solvent was diluted with demineralized water to reach the targeted concentration of 27 wt% of AMP and 13 wt% of PZ (AMP/PZ ratio of 2.1). The actual concentrations of AMP and PZ after dilution were respectively 25.37 and 12.41 wt%. The amine concentration has been adjusted continuously over the test campaign, depending on operating conditions, to maintain the amine concentration. The amine plant has been operated for more than 1500 hours until the 10th of January. The test plan has been adjusted throughout the campaign based on the results and may be found in Table 1. In every test, the flue gas flow rate and solvent flow rate were kept constant and the steam flowrate was adjusted to reach the targeted capture rate.

The test campaign started with the phase A at 90% capture rate. The tests were run with a flue gas temperature at the absorber inlet of 30°C, 24 meters of packing in the absorber. Phase B was a repeat of phase A with a higher capture rate, targeted at 98%. Precipitation was observed in the lower section of the absorber because of low flue gas temperature and high CO_2 loading in the rich solvent (see section 3.2). As the flue gas temperature affects the capture plant thermal performance, tests from phases A and B were repeated later with a flue gas temperature at 40°C (respectively phases AA and BB).

Performance tests with 18 m of packing were carried out with a flue gas at 40°C in phases C and D, respectively at 90 and 98% capture rates. Tests with 12 m of packing were conducted in phase E with 90% of CO_2 captured. A higher capture rate was not achievable here due to maximum capacity of the CHP reboiler and the CHP stripper.

Table 1. Operational parameters for the TCM ALIGN-CCUS test campaign and the MEA test cases MEA 2 and MEA Base [2, 4]. Stripper pressure was set at 0.9 barg except for the F series where it varied from 0.5 to 1.6 barg.

#	Abs. pack [m]	Flue gas x 1000 [Sm^3/h]	Flue gas temperature [°C]	CO_2 wet abs inlet %	L/G [kg/Sm^3]	CO_2 Capture %
A	24	50 - 59	30	~ 3.5	0.6 – 1.2	90
AA	24	50 - 60	40	~ 3.5	0.6 – 0.9	90
B	24	50	30	~ 3.5	0.7 – 1.2	98
BB	24	50-59	40	~ 3.5	0.7 – 0.9	95-98
C	18	50 - 59	40	~ 3.5	0.7 – 1.2	90
D	18	50	30-40	~ 3.5	0.7 – 1.2	98
E	12	50	40	~ 3.5	0.8 – 1.3	90
K	18-24	59	40	~ 3.5	0.6 – 0.8	85
F	18	59	40	~ 3.5	0.7	90
MEA 2	24	47	30	3.6	0.9	87
MEA Base	24	59	30	3.6	1.0	84

In phase F, the plant was operated with 18 m of packing and 90% capture rate, at the optimal liquid-to-gas ratio (L/G) from phase C tests. The purpose was here to assess the effect of the stripper pressure on the energy penalty of CESAR1 solvent. Working at higher pressure is beneficial for the CO_2 compression step. The downside might be a higher degradation rate of the solvent provoked by the higher temperature in the reboiler.

The purpose of phase K was to compare the CESAR1 performance against MEA baseline conducted in TCM amine plant [4]. The operating conditions were kept as close as possible to MEA tests to make the comparison more relevant, except the flue gas temperature. Those tests were carried out with 18 and 24 meters of packing, while MEA baseline was at 24 meters. TCM amine plant has been designed to be flexible, based on generic MEA solvent. Compared to MEA, the optimum L/G ratio with CESAR1 is lower due to its higher working capacity. The optimized operating conditions with CESAR1 were found to be very close to the limit of the operating window of the stripper due to very low amine circulation rate and hence low wetting of the packing. The amine pumps and stripper are oversized for this type of solvent. The best performances are achieved at the minimum flowrate delivered by the amine pumps (35,000 kg/h) and below the turndown capacity of stripper. The CHP stripper is designed for a minimum liquid flow rate of 42,000 kg/h. Hence, the performance may be affected by the plant design.

TCM used the same calculation method to assess the performance of the CESAR1 solvent as in [2] that also presents a detailed description of the methodology and the instruments used. The capture rate is calculated over the absorber. The energy demand is based on the energy brought to the reboiler and is called the specific reboiler duty (SRD).

2.3. Results from tests at 90% capture rate

Figure 2 shows the energy consumption required to capture 90% of the CO_2 from the CCGT flue gas. The best performance is achieved with 24 m of packed bed. The plot shows better results with flue gas temperature at 30°C compared to 40°C (A vs AA series). The minimum steam consumption is around 3.1 MJ/kg CO_2 which is significantly lower compared to 30 wt% MEA solvent tested at TCM. The optimum is found at the lowest L/G ratio, i.e. 0.7 kg/Sm^3.

The steam consumption increases by approximately 15% when the flue gas temperature goes up to 40°C. However, the plant cannot be operated at 30°C for a long period of time because of precipitation of CESAR1 solvent in the absorber. The energy consumption is partially dependent on flue gas temperature, this indicates a room for improvement either by adjusting the flue gas temperature and/or the amine concentration.

Reducing the packing height from 24 to 18 meters does not impact the steam demand (AA vs C series). The upper 6 meters of packing are not necessary to capture 90% of the CO_2. With a shorter absorption section (12 meters, E series), the energy demand increases significantly. The SRD at optimum conditions is 25% higher, corresponding to an L/G ratio between 1.0 and 1.1 kg/Sm^3. A short absorption column is not suitable to achieve low energy consumption but may be beneficial for projects where cheaper thermal energy is available or lower CO_2 capture rate is targeted. CESAR1 results are compared to TCM operation with 30% MEA at 47,000 Sm^3/h flue gas flow [2], see also Table 1. The left part of Figure 2 shows that operation with CESAR1 resulted in lower SRD values at lower liquid to gas ratios compared to the MEA 2 case. The right part of Figure 2 shows CO_2 concentration into the absorber and lean amine loading. The AA and MEA 2 cases are at a higher CO_2 level than the other cases. Lean loading is, as expected, decreasing for decreasing L/G ratios.

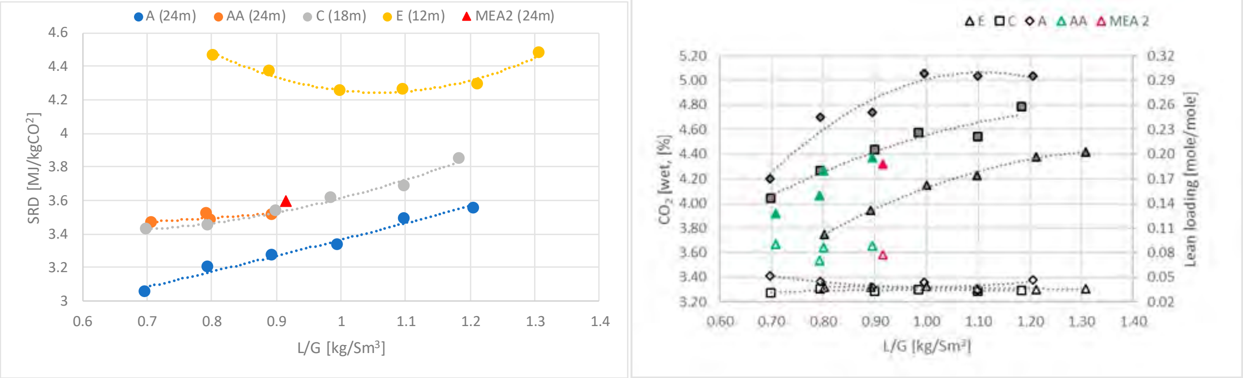

Figure 2. Left: Specific reboiler duty versus liquid to gas ratio for CESAR1 test series and MEA 2. The CO_2 capture rate is around 90% and flue gas flow into the absorber 50,000 Sm^3/h. Case A and MEA 2 are with 30°C flue gas temperature while rest of the cases are at 40°C – Right: CO_2 concentration (wet) into the absorber and lean amine loading for CESAR1 test series and MEA 2 [2]. Open symbols are for CO_2 concentration and left y-axis and filled symbols for lean loading and right y-axis.

2.4. Results from tests at 98% capture rate

Figure 3 shows the energy demand to achieve 98% capture rate. The lowest energy consumption is achieved with flue gas at 30°C and 24 meters of packing (B series). Operating conditions being very close to A series, precipitation was also experienced. Flue gas temperature was adjusted to 40°C (BB series) leading to a 15% higher steam consumption. The optimum case in BB series is not found at the lowest L/G ratio, but at 0.8 kg/Sm^3. With an absorption section of 18 meters, contrary to the 90% capture rate cases, the energy demand is slightly higher. With an absorption section of 12 meters, the 98% capture rate was not achieved. The limitation is coming from the lean loading. The lean solvent is not lean enough to reach such a high capture rate despite the maximum steam flow rate in the reboiler.

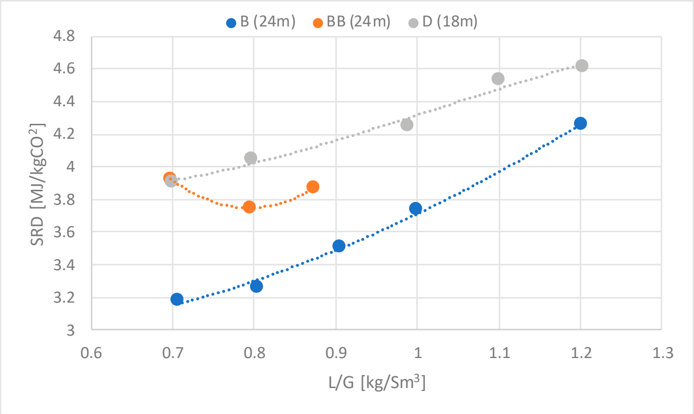

Figure 3. Specific reboiler duty versus liquid to gas ratio for CESAR1 test series B (blue), BB (orange) and D (grey). The CO_2 capture rate is around 98% and flue gas flow into the absorber 50,000 Sm^3/h. Case B is with 30°C flue gas temperature while the rest of the cases are at 40°C.

2.5. Variation of capture rate

The energy needed to capture either 85% or 90% of CO_2 is very similar as shown in Figure 4. This observation is valid at both packing heights (18 or 24 meters). There is a gap in energy consumption to reach 98% capture rate regardless the packing heights. However, it might still be acceptable in some cases where high capture rates are targeted. The increase in SRD to reach 98% capture rate is in the range 5-15% compared to 90% capture rate cases. The gap is larger with a shorter absorption bed (18 meters). While the capture rate in many projects was set around 90%, there is a new tendency to increase it above 95% and minimize the CO_2 emitted [5]. The CESAR1 solvent shows a good ability to reach this target with a limited extra steam consumption. In Figure 4, CESAR1 tests are also compared to MEA base [4] which was operated at 30% MEA. The K-series and MEA base were operated at 59,000 Sm^3/h flue gas flow, 24-meter absorber packing and at around 85% capture rate. The K series resulted in lower SRD values than MEA base at lower L/G ratios. Figure 5 shows corresponding values for CO_2 concentration into the absorber and lean CO_2 loading. The CO_2 concentration was constant in CESAR1 tests around 3.4% while it was higher in MEA base. Higher the CO_2 concentration lower the energy demand.

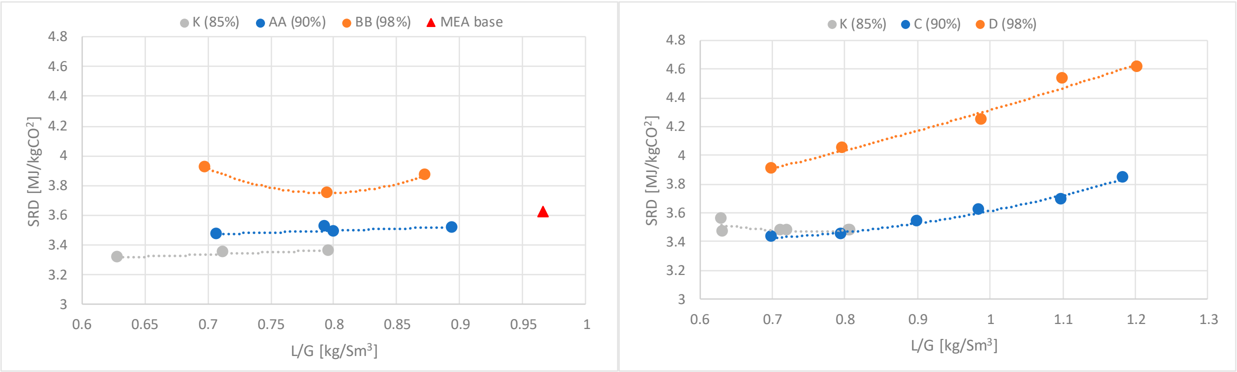

Figure 4. Specific reboiler duty versus liquid to gas ratio for CESAR1 tests and MEA base at 30% amine concentration [4]. The left figure shows results at 24 meters of packing while the right figure shows results at 18 meters of packing. Flue gas flows into the absorber in case K and MEA base are 59,000 Sm^3/h while rest of the cases are at 50,000 Sm^3/h. Capture rate varies from 85% to 98%.

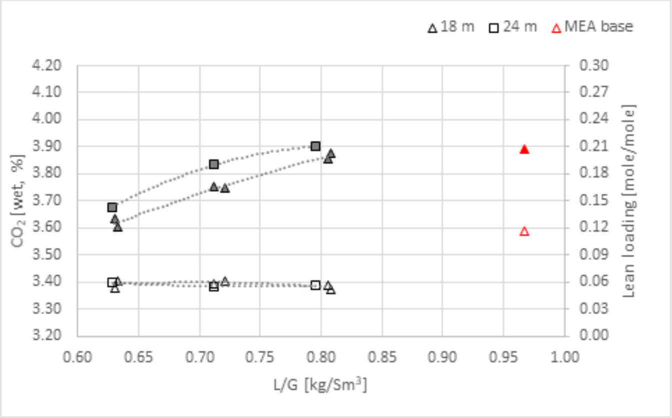

Figure 5. CO_2 concentration (wet) into the absorber and lean amine loading for test series K (black) and MEA base (red) [4]. Open symbols are for CO_2 concentration and left y-axis and filled symbols for lean loading and right y-axis.

2.6. Stripper pressure tests

Based on results from phase C (18m of packing, 90% capture rate), the phase F was carried out to assess the effect of the stripper pressure on the performances. From a solvent management point of view, it is better to run the stripper at low pressure to reduce the stripper bottom temperature and hence, reduce the thermal degradation rate of the solvent. On the CO_2 transport side, getting the CO_2 at a higher pressure will be beneficial to reduce both Capex and Opex for CO_2 compression. Based on optimal conditions from phase C, the stripper pressure was varied from 0.5 up to 1.6 barg. The flue gas flowrate was increased to 59,000 Sm^3/h while keeping the L/G ratio at 0.7 kg/Sm^3. This change in flue gas flow rates aims at increasing the liquid flow rate and improve the vapour-liquid traffic in the stripper, while remaining within the stripper overhead capacity. The specific reboiler duty presented in Figure 6 is plotted against the stripper pressure. The minimum energy consumption is found at 1.2 barg, where the stripper bottom temperature is 124°C, which might seem acceptable. However, long term tests are needed to quantify its effect on solvent degradation and consumption together with corrosion.

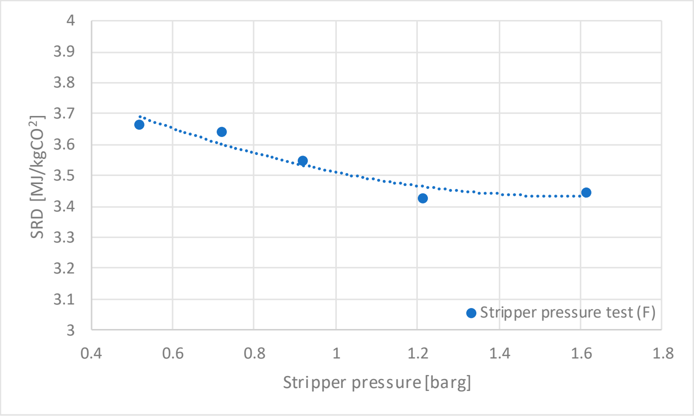

Figure 6. Specific reboiler duty versus stripper pressure. Flue gas flow into the absorber is 59,000 Sm^3/h with 18 meters of packing and 90% capture rate.

2.7. Solvent Management

In addition to the energy consumption, another important parameter to assess the performance of an amine-based capture technology is the solvent consumption. There are two main sources of solvent loss, one is from degradation, the other one is from emission to the atmosphere from the absorber stack. The solvent consumption depends mainly on the flue gas composition and impurities and on the operating conditions. An investigation of solvent degradation and emissions from TCM amine plant operated with MEA has previously been published [6]. The solvent loss during the CESAR1 campaign is based on parametric testing and might not represent the solvent loss for relatively stable operations applicable to commercial plants.

The thermal and oxidative degradation mechanisms for AMP and PZ have been explored separately [7-9]. According to the literature, the most common PZ degradation products are Piperazinol, Ethylene diamine (EDA), 2-oxopiperazine (OPZ), N-formyl piperazine (FPz), N-methylpiperazine (MPZ), Aminoethyl piperazine (AEP), Mononitrosopiprazine (MNPZ), Acetate, Oxalate, Ammonium, Ethylpiperazine (EPZ) and Ammonia. Other minor products include carboxylate ions, amides, glycolate, nitrite and nitrate. Most common AMP degradation products are 4, 4-dimethyl-2-oxazolidinone (DMOZD), 2, 4-Lutidine, Acetone and Formic acid.

The main areas of plant that facilitate degradation for any amine in post-combustion CO_2 capture process are absorber sump, cross heat exchanger, reboiler, and reclaimer [7]. Thermal and oxidative degradation occur mainly due to the high temperature of the process, in the presence of dissolved oxygen, metals and free radicals [7].

With CESAR1 solvent, PZ was observed to be the most degraded amine. The main reaction was between NO_2 coming from the flue gas and secondary amine functionality of the PZ to form Nitrosopiperazine. Nitrosamine concentration in the solvent has increased constantly through the campaign. Nitrosamines were not released in the stripper. Solvent reclaiming is the only way to wash them out. However, as long as the solvent performance are not affected, there is no specific risk associated to run the plant with non-volatile nitrosamines. Other degradation products include formic acid which was the major degradation product (see Figure 7) among the small chain organic acids. For the detailed analysis of solvent loss due to degradation and emission, the campaign was divided into Period 1 and 2. Duration for Period 1 with low NO_2 (0.5 ppmv) was September 12, 2019 to October 12, 2019 and Period 2 with high NO_2 (2.35 ppmv), was from October 12, 2019 to November 1, 2019). The NO_2 concentration in Period 2 is considered high and was the result of no ammonia feed to the Selective Catalytic Reduction of NOx (SCR) in the CHP plant, upstream the amine plant.

A comprehensive lab schedule was set up, covering all analysis needed to follow up on the performance of the plant, emissions, corrosion and degradation. Samples were taken from lean amine and chemical analysis of the samples were performed to analyze the solvent condition. The calculations were based on wt% CO_2, wt% AMP, wt% PZ, water content (Karl Fisher), degradation products and heat stable salts (HSS). The most common amine strength titration method (Total alkalinity) was developed for amine solutions with no contaminants. Non-volatile degradation products (DMOZD, 2,4 Lutidine, MNPZ, OPZ) were quantified and the formation and total accumulation determined for Period 1 and Period 2 are presented in Figure 7 and Table 2. The rates of formation of MNPZ and OPZ have increased in Period 2 as compared to Period 1, due to the increased NO_2 concentration. Inventory variation for the testing period of Period 1 and Period 2 was evaluated based on the changes in total solvent alkalinity. Possible unquantified degradation products are formylpiperazine (FPZ), Acetylpiperazine (APZ) and unknown products with molar masses 55.057, 56.05 and 57.06 gram/mol were detected by PTR-ToF-MS. Further investigation would be needed to allow for quantification. Other factors include high levels of NO_x and oxidative degradation catalyzed by increased iron concentration. Iron catalysis may also affect the formation of total formate and ammonia (both increase with increase in iron concentration) [8]. Alkalinity balance decreases as well with the increase in the concentration of iron in the solvent.

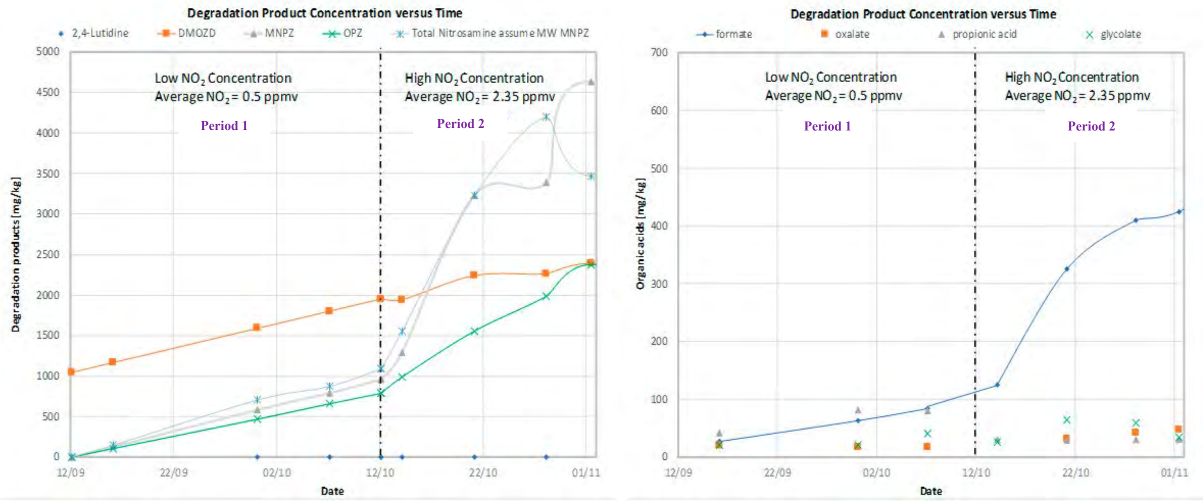

Figure 7. Degradation product concentration in Period 1 and Period 2 during CESAR-1 testing campaign (left). Degradation product concentration versus time showing increase in the concentration of formic acid or formate in Period 2 (right).

Table 2. Total amine losses (emissions + degradation)

Parameters	Units	Period 1	Period 2
Amine loss (Degradation products)	kg	87.04	356.90
CO_2 captured	kg	1971.68	2112.05
Amine loss per ton of CO_2 captured	kg amine/ton CO_2	0.044	0.169
Total ammonia emissions to stack	kg/hr	0.11	0.17
Total aldehyde emissions to stack	kg/hr	0.029	0.035
AMP emissions to stack	kg	135.2	68.3
PZ emissions to stack	kg	2.8	1.5
Total amine loss to stack / ton of CO_2	kg amine/ton CO_2	0.070	0.033
Total Amine loss per ton of CO_2 captured (emissions + Degradation)	kg amine/ton CO_2	0.114	0.202

Atmospheric emissions were monitored throughout the campaign and are reported in a separate publication [10]. For the entire campaign, the piperazine emissions were in low ppb levels, even under high emissions testing. AMP emissions were in the range of 0.3 ppm to 2 ppm for standard U-curve tests, with high emissions tests yielding emission levels in the range of 6-9 ppm (e.g. reduced water wash efficiency). Nitrosamines were not detected in absorber stack even at ppb level. This topic will be addressed in an upcoming paper.

Based on emission and degradation, the average solvent loss has been estimated to be 0.16 kg amines/ton of CO_2 for CCGT type of flue gas. This number represents 1600 hours of operation with a lot of parameters variating and it is considered to be in the low range of amine solvent loss. Similar or higher numbers were reported from test campaigns carried out at TCM [6, 11], e.g. MEA consumption was estimated around 1.5 kg amines/ton of CO_2 during TCM MEA-2 campaign.

Successful solvent management includes setting strict threshold limits for the key indicators and applying reclaiming to keep the solvent as clean as possible. Proper solvent management has the potential to control solvent degradation and emissions and thus lower solvent consumption and reduce maintenance needs. From TCM's operational experience, good solvent hygiene can be achieved by closely monitoring physical appearance of the solvent, together with degradation and emissions. An increase in ammonia emission will give a direct indication of solvent degradation and factors like NO_x concentration in the flue gas and iron content can have a huge impact on solvent degradation. The solvent should be clear, light in color and the solvent mass balance should be closed. It is important to keep the solvent fresh, with low concentrations of degradation and corrosion products. Other important measures to improve the solvent hygiene can be solvent reclaiming.

3. Operational experience

3.1. Lab experiments, solvent supply and limits for operation.

A set of laboratory experiments were carried out prior to purchase of solvent for three different purposes:

- Determine if the solvent components (AMP and PZ) should be ordered separately or pre-mixed.
- Supply information about solvent behavior and if it precipitates at various CO_2 loading and temperature.
- Study at which levels of CO_2 loading and temperature precipitation occurs.

For the first purpose, samples of 90% AMP, 68% PZ and a mixture with 53% AMP and 28% PZ were exposed to different temperatures. Piperazine precipitated when exposed to temperatures below 50°C. AMP and the AMP/PZ mixture samples did not form precipitate above 7°C. Based on the results, it was recommended to order the blend pre-mixed to avoid precipitation of pure piperazine in the solvent storage system.

For the second purpose, the AMP/PZ mixture was diluted to 27% AMP and 14% PZ and three samples of the mixture were prepared: one rich (0.73mole CO_2/mole amine), one lean (0.10 mole CO_2/mole amine) and one unloaded. These samples were each divided in three and exposed to 4°C, 25°C and 40°C. Precipitation occurred in all three rich samples and gel formed in the lean and unloaded samples at 4°C. The samples at 4°C are depicted in Figure 8, showing the two different changes observed in the samples at high, low and no loading. Further, the rich solvent sample was diluted with unloaded CESAR1 solvent to study closer at which levels of CO_2 loading and temperature precipitation occurs. The results from the experiments with varying loading and temperature are given in Table 3. Overall, these experiments show that, at low loading, the solvent form a gel at low temperatures, while precipitation occurs at high loading and especially in combination with low temperatures. At the highest loading, precipitation occurs at all temperatures. An additional test was conducted on some of the samples to attempt to reverse the precipitation and gel formation. The gel vanished after heating to 40°C. All rich samples with 0.73 moles CO_2/mole amine were heated to 55°C. The precipitate in these samples was not dissolved.

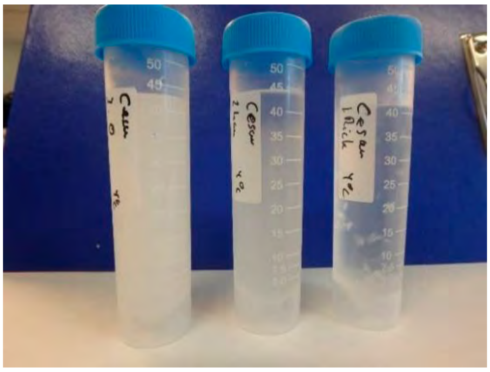

Figure 8. Samples of unloaded, lean (0.1 moles CO_2/mole amine) and rich (0.73 moles CO_2/mole amine) CESAR1 solvent at 4°C.The unloaded (left) and lean (middle) solvent form a gel, while precipitation is observed in the rich (right) sample.

Table 3. Overview of observations made during the experiments where samples of different loading were exposed to different temperatures.

Loading [mole CO_2/mole amine]	Observation @40°C	Observation @25°C	Observation @23°C	Observation @7°C	Observation @4°C
0.73	Little precipitation	Some precipitation			Some precipitation
0.61	No precipitation		No precipitation	Precipitation after 48 hours	
0.50	No precipitation		No precipitation	No precipitation	
0.39	No precipitation		No precipitation	No precipitation	
0.29	No precipitation		No precipitation	No precipitation	
0.10	No precipitation	No precipitation			Gel formation (~80%)
0.00	No precipitation	No precipitation			Gel formation (~100%)

The mixed solvent was delivered at 72% amine concentration. As lab test showed gel formation in lean and unloaded solvent at low temperatures, the solvent was delivered at 40°C and storage tank temperature maintained at 45°C by circulating and heating the solvent. The plant was initially filled with solvent from the storage tank. Make-up from the tank has been added when needed. The lines from the tank to the plant have freeze protection but are not heated. To avoid gel formation in these lines, flushing with water after any transfer from tank to plant has been a part of the filling procedure. Even with water flush after each transfer, there have been some issues with plugging of the line. One part of the line is not possible to flush, and this is believed to be the cause of the plugging. Dilution of the solvent in the tank has been suggested as a mitigating action in order to reduce the risk of plugging the line.

The lab experiments indicate that both high loading and low temperatures should be avoided during operation. The main concern in case of precipitation was blocking of heat exchangers. The lab results were considered when operating the plant for parametric testing and during periods with standstill while the solvent was stored in the plant. The density measured on both lean and rich solvent flows could give indications of loading and the changes in density were monitored during the campaign.

3.2. Precipitation in absorber packing and mitigating actions

During phase A, the differential pressure in the lower absorber packing increased, as shown in Figure 9. The measured differential pressure is compared to a theoretical value for a given flue gas and solvent flow rate based on previous TCM experimental data. Lean solvent samples were analyzed for amine concentration and the amount of amine in the plant was calculated. The decrease in amines indicated that solvent was lost from the process and the plant was thoroughly checked for leakage without any findings. In the majority of the cases, the amount of amine in the plant is decreasing with increasing differential pressure, most significantly during phase B (98% capture rate). The increased differential pressure was then suspected to be caused by precipitation in the lower absorber packing. Phase B was followed by repetition of cases from phase A with higher solvent flow and lower capture rate than phase B, resulting in a decrease in the differential pressure. A mitigating actions test (MitAct in Figure 9) was done at higher solvent flow rate with increased lean solvent and flue gas temperatures to investigate if the differential pressure could be further reduced. After the mitigating actions test, the B1 test was repeated to verify the impact on the amine mass. Solvent analysis confirmed a significant increase in the amine mass compared to B1 (at the start of phase B), indicating that the lost solvent was precipitation that had been dissolved. As the differential pressure was still higher than the theoretically expected value, a long flushing without flue gas flow to the absorber was done. After the flushing, the differential pressure was back to the theoretically expected value and the amount of amine in the plant back to similar value as at the start of the campaign. It has been calculated that 5.7 tons of amines were precipitated at the end of phase B. This corresponds to roughly 29% of the total amine mass. In order to reduce the risk of precipitation in the absorber, the rest of the planned tests were operated at 40 °C flue gas inlet temperature. It can be observed that there is no differential pressure increase during the first InsVal (Instrument Validation) test, which was also operated with 40 °C flue gas inlet temperature.

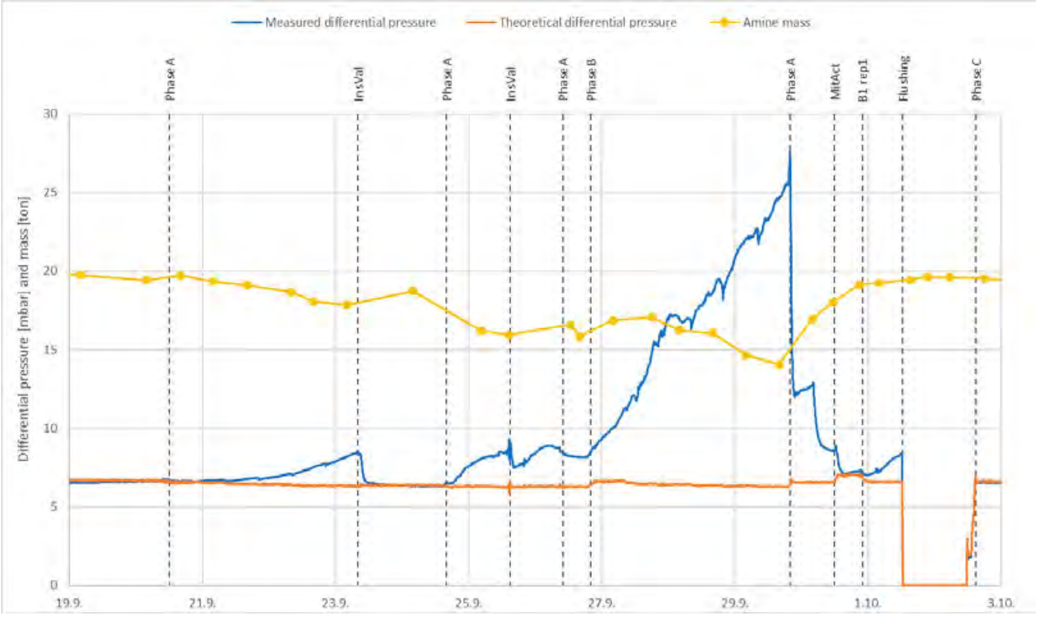

Figure 9. Total amine mass in the plant (yellow), measured (blue) and theoretical (orange) differential pressure in the lower absorber packing.

The density of the solvent, measured on lean and rich flow, did not indicate that precipitation should have been occurring during these initial phases. It is suspected that local differences in loading and temperature in the absorber can give local precipitation. Monitoring of the differential pressure in the absorber packing is recommended. Precipitation is believed to be caused by PZ. However, both AMP and PZ seem to precipitate as their ratio was kept constant during the precipitation periods.

4. Conclusions

The ALIGN-CCUS test campaign was the first TCM test campaign with CESAR1 solvent. The main objective of the campaign was to assess the performance of the solvent in terms of energy demand, emissions and solvent consumption. Some operational challenges have been experienced throughout the test campaign. The CESAR1 solvent is known to have better performance than MEA in terms of thermal energy and stability. This has been confirmed during this test campaign. The energy demand is lower by around 10% compared to 30 wt% MEA. However, the comparison is not straightforward. The MEA baseline was conducted before the rich bypass stream was implemented. In addition to the difference in amine concentration, PZ has two amine functions and can act as a promoter. 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. It would be interesting to investigate mitigating actions to be able to lower the gas temperature. Although they were higher than in MEA case, the atmospheric amine emissions were kept low throughout the test campaign (below 1 ppmv). The high vapor pressure of AMP was the main cause of emissions. PZ emissions were found to be negligible with CCGT flue gas but could be strongly influenced by the presence of aerosols. The solvent consumption was found to be lower than MEA. The main loss comes from degradation. The PZ is very sensitive to NO_2, it reacts to form nitrosamines. The nitrosamine concentration was high in the solvent but none of them were found in the absorber stack. The HSS concentration was kept low. The test campaign was successful and gave TCM valuable learnings.

Acknowledgements

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CATCHING OUR FUTURE

Results from CESAR-1 Testing with Combined Heat and Power (CHP) Flue Gas at the CO_2 Technology Centre Mongstad

(2021)

TCCS-11 - Trondheim Conference on CO_2 Capture, Transport and Storage
Trondheim, Norway - June 21–23, 2021

RESULTS FROM CESAR-1 TESTING WITH COMBINED HEAT AND POWER (CHP) FLUE GAS AT THE CO_2 TECHNOLOGY CENTRE MONGSTAD

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Abstract

CO_2 Technology Centre Mongstad (TCM) houses a demonstration-scale test facility for CO_2 capture solvents termed the "amine plant," where multiple test campaigns have been performed on numerous solvents that the owners of TCM, TCM DA, have conducted since its inauguration in 2012. The large number of public, industrial, research, and academic participants involved in these campaigns have enriched the projects and ensured that the significant results serve a broad audience. The main objective of these campaigns was to produce knowledge that can be used to reduce the cost as well as the technical, environmental, and financial risks for the commercial-scale deployment of post-combustion CO_2 capture (PCC). This includes demonstration of a model-based control system, dynamic operation of the amine plant, investigation of amine aerosol emissions, and establishment of the baseline performance with monoethanolamine for residual fluid catalytic cracker (RFCC) and combined-cycle gas turbine (CCGT)-based combined-heat-and-power plant (CHP) flue gases. The RFCC flue gas is sourced from a nearby Equinor refinery that emulates coal flue gas in composition with 13%–14% vol CO_2 content and the CHP flue gas represents flue gas from CCGT power plants with a 3.5% vol CO_2 content. In addition to baseline testing, specific tests targeted at reducing CO_2 avoided cost have also been conducted utilizing both flue gas sources. This paper focuses on the testing of the CESAR-1 solvent, a blend of 2-amino-2-methyl-1-propanol and piperazine.

The Electric Power Research Institute, Inc. (EPRI) assessed the performance of the process using an independent verification protocol (IVP) developed previously. The IVP provides a structured testing procedure for assessing the thermal and environmental performance of PCC processes under normal operating conditions. Throughout the CESAR-1 testing, TCM manually collected extractive samples from the depleted flue gas and product CO_2 outlets sequentially. As part of the IVP, EPRI also assessed critical plant instrumentation at TCM for accuracy and precision error based on a comparative analysis done during testing operations and against calibration checks.

The CESAR-1 process was evaluated during 16 individual test periods over four days in June 2020. During the tests, extractive samples were taken to measure process contaminants such as aldehydes, ketones, amines, and ammonia. Sulfur oxides and nitrogen oxides were continuously monitored using Fourier-transform infrared (FTIR) analysers on the depleted flue gas and product CO_2 streams. TCM has installed multiple measurements (FTIR, non-dispersive infrared sensor, and gas chromatography) of the CO_2 concentration allowing comparative confirmation during the test periods. The capture rate was calculated via four methods along with evaluation of the CO_2 recovery, which is indicative of the overall mass balance. The overall thermal performance (energy consumption) was assessed based on measured data taken during each of the sampling periods. The CO_2 capture rate achieved during the CESAR-1 testing was 97–99%, with steam reboiler duties of 3.41–3.54 GJ/tonne-CO_2, and the CO_2 gas mass balance closures were close to 100%. These data and the associated assessments, along with the results of TCM sampling during these tests, are presented in this paper.

Keywords: *CO_2 capture; EPRI; Post-combustion capture; CO_2 Technology Centre Mongstad; TCM; CESAR-1*

1. Introduction

The CO_2 Technology Centre Mongstad (TCM) is located next to the Equinor refinery in Mongstad, Norway. TCM DA is a joint venture owned by Gassnova representing the Norwegian state, Equinor, Shell, and Total. TCM is home to one of the largest post-combustion CO_2 capture (PCC) test centers in the world. This facility entered the operational phase in August 2012 and is dubbed the "amine plant."

A unique aspect of the facility is that either a flue gas slipstream from a natural gas-fired combined-heat-and-power (CHP) plant or an equivalent volumetric flow from a residual fluid catalytic cracker (RFCC) unit can be used for CO_2 capture. The CHP flue gas contains about 3.5 vol% CO_2 and the RFCC flue gas contains about 13–14 vol% CO_2, the latter of which is comparable to CO_2 levels seen in a coal-fired flue gas. The amine plant, designed and constructed by Aker Solutions and Kværner, is a highly flexible and well-instrumented facility that can accommodate a variety of technologies with capabilities of treating flue gas streams of up to 60,000 Sm^3/hr.

The plant is offered to developers of solvent-based CO_2 capture technologies to test the performance of their solvent technology and to verify systems aimed to reduce the atmospheric emissions and environmental impact of solvent emissions and degradation products from these processes.

The objective of TCM DA is to test, verify, and demonstrate CO_2 capture technologies suitable for deployment at full scale. A significant number of vendors, including Aker Solutions, Alstom (now GE Power), Cansolv Technologies Inc., and Carbon Clean Solutions Ltd., have already successfully tested using the TCM DA facilities to assess their CO_2 capture technologies.

Multiple tests using the CESAR-1 solvent have been carried out at TCM to define the baseline performance of the solvent for defined operating conditions using CHP flue gas boosted to 5 vol% CO_2 content using recycle in accordance with an independent verification protocol (IVP), which provides a structured testing procedure, developed by the Electric Power Research Institute, Inc. (EPRI) [1]. These tests are compared with prior MEA testing at TCM using the CHP flue gas without recycle at 3.5 vol%.

2. Amine Plant

The TCM 234 tonnes-CO_2/day amine plant was designed to be flexible to allow testing of different configurations. The amine plant is configured to remove CO_2 from a natural gas-fired combustion turbine-based CHP plant flue gas or a RFCC off-gas. The typical characteristics of these two flue gas streams are shown in Table 1.

Table 1**:** Nominal characteristics of flue gas supplied to TCM

Parameter	Units	CHP Flue Gas	RFCC Flue Gas
Temperature	°C	185	27
N_2+Ar	% vol, dry	81.5	82.5
O_2	% vol, dry	14.8	4.3
CO_2	% vol, dry	3.7	13.2
SO_2	ppmv, dry	very small	20 to 60
NO	ppmv, dry	<5	50 to 115
NO_2	ppmv, dry	<0.5	3
SO_3	ppmv, dry	very small	7 to 10*
CO	ppmv, dry	-	0 to 3
NH_3	ppmv, dry	<5	1
Particulates	mg/Nm^3	very small	14 to 41*
Chloride	mg/Nm^3	-	< 0.1

** controlled via candle filter*

For these tests, a portion of the product CO_2 was recycled to the CHP flue gas inlet stream in a controlled way to maintain the incoming CO_2 concentration at 5% vol, dry. A process flow diagram showing high-level equipment contained within the amine plant along with key existing instrumentation is shown in Figure 1.

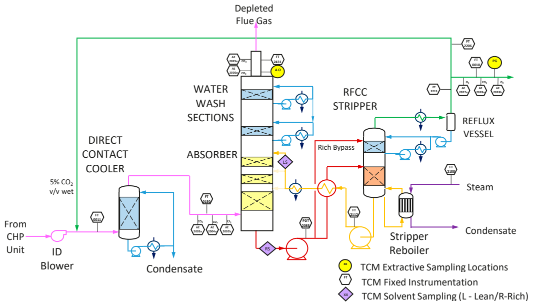

Figure 1**:** Process flow diagram for the TCM amine plant with CO_2 recycle

Major systems include:

- An induced draft (ID) blower to overcome pressure drops and blow the flue gas through the plant with an output capacity of up to 270 mbar and 70,000 Sm^3/hr.
- A direct-contact cooler (DCC) system to initially lower the temperature of and saturate the incoming flue gas by a counter-current water flow to improve the efficiency of the absorption process and provide pre-scrubbing of the flue gas. The DCC system has two individually operated packed columns for operations with the CHP flue gas and the RFCC flue gas, respectively. The DCC column designed for CHP gas operations is 3-m diameter and a total 16 m height. The section where water counter currently contacts the flue gas is 3.1 m high with Flexipac 3X structured stainless-steel packing of Koch Glitsch.
- An absorber to remove CO_2 from the flue gas. The absorber has a rectangular, polypropylene-lined concrete column with a 3.55 x 2 m cross-section and a total height of 62 m. The lower regions of the tower, where the amine solution contacts the flue gas, consist of three sections of Koch-Glitsch Flexipac 2X structured stainless-steel packing of 12 m, 6 m, and 6 m of height, respectively. Water-wash systems are located in the upper region of the tower to scrub and clean the flue gas, particularly of any solvent carry over, and consist of two sections of Koch-Glitsch Flexipac 2Y HC structured stainless-steel packing, each 3 m in height. The lower water-wash section is used to cool the depleted flue gas for overall plant water balance by adjusting the temperature of the circulating water. The uppermost water-wash section was operated as an adiabatic acid-wash stage for further emission mitigation. Liquid distributors, liquid collector trays, and mesh mist eliminators (Koch-Glitsch) are located at various locations in the tower, and the final mesh mist eliminator at the top of the tower is by Sulzer. The CO_2 depleted flue gas exits the absorber column to the atmosphere through a stack located at the top of the column.
- Stripper columns to recover the captured CO_2 and return CO_2-lean solvent to the absorber. The amine plant consists of two independent stripper columns with a common overhead condenser system. The two stripper columns are operated independently considering the CO_2 content in the flue gas due to column design, hydraulics, and gas velocity effects. The smaller diameter stripper column is used when treating CHP flue gas or RFCC gas

diluted with air, whereas the larger diameter column is used when treating flue gases of undiluted (i.e., higher CO_2 content) RFCC gas or when operating with CHP using CO_2 recycle, as is the case with these tests. The CHP stripper is 1.25 m in diameter and 28 m in height tangent-to-tangent. The RFCC stripper is 2.2 m in diameter and is also 28 m tangent-to-tangent. The lower regions of both stripper columns, where the amine solution is stripped, consist of Koch-Glitsch Flexipac 2X structured stainless-steel packing 8 m high. The upper regions of the strippers consist of a rectifying water-wash section of Koch-Glitsch Flexipac 2Y HC structured stainless-steel packing 1.6 m high. Liquid distributors, liquid collector trays, and mesh mist eliminators (all by Koch-Glitsch) are located at various locations in the strippers. Each stripper column is connected to its respective steam-heated reboiler, providing the necessary heat required for the stripping process. Both strippers circulate solvent to the reboilers by thermosiphon. The RFCC stripper also has a circulating pump to assist at low-load operation and during startup. The RFCC reboiler is a shell-and-tube arrangement and the CHP reboiler is a plate-in shell heat exchanger.

- A lean-solvent trim cooler that uses seawater to cool the lean solvent leaving the cross heat exchanger to a desired temperature before admission to the absorber column.
- A set of pumps used to move the CO_2-lean and CO_2-rich solvent streams between the absorber and stripper and through a cross heat exchanger to recover heat from the lean stream.
- A reflux drum, condenser, and pumps to dry the product CO_2 that exits the stripper. A portion of the product CO_2 can also be recycled back to the inlet of the CHP DCC to increase the concentration of the CO_2 in the inlet flue gas stream when using CHP flue gas.

The TCM facility can test virtually any PCC solvent-based process as the amine plant has been designed to accommodate a variety of technologies. The facility also has excellent instrumentation and an on-site lab for detailed analysis.

An IVP was developed to be used as part of the overall performance assessment of amine-based processes and has been updated over time to apply to either CHP or RFCC operation on the TCM amine facility. The IVP is designed to provide a structured testing procedure for assessing thermal and environmental performance of PCC processes under normal operating conditions. Uncertainty for key flow measurements was carried out as part of the IVP previously [2].

3. CESAR-1 CHP Campaign Overview

The CESAR-1 solvent is a blend of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ). CHP flue gas capture performance assessment periods were conducted in June 2020. During the testing, personnel from TCM manually collected extractive samples from the depleted gas outlet and the product CO_2 line downstream of the RFCC stripper. In previous tests, this was sometimes performed by an independent testing contractor. However, TCM's competency related to performing this testing was deemed adequate by EPRI during prior monoethanolamine (MEA) baseline campaigns, especially since TCM is not commercially involved in the outcome and hence can be considered to be unbiased.

Data logs for all sampling periods containing pertinent flows, temperatures, pressures, and concentrations measured by permanent plant instruments were supplied by TCM for the entire test period. The sampling time periods, and sampling period designators are shown in Table 2 along with additional sampling undertaken on each day.

Table 2**:** CESAR-1 CHP sampling periods

Date	#	Time	Stream	Samples
June 24, 2020	1	9:26–11:39	CO_2	AMP, PZ, NH_3
	2	11:45–12:27	CO_2	Aldehyde/Ketones
	3	12:15–12:25	ABS	Aldehyde/Ketones
	4	12:48–13:48	ABS	AMP, PZ, NH_3
June 25, 2020	5	10:16–12:16	ABS	AMP, PZ, NH_3
	6	10:32–12:37	CO_2	AMP, PZ, NH_3
	7	12:28–12:58	ABS	Aldehyde/Ketones
	8	12:43–13:20	CO_2	Aldehyde/Ketones
June 26, 2020	9	9:33–11:33	ABS	AMP, PZ, NH_3
	10	9:43–11:50	CO_2	AMP, PZ, NH_3
	11	11:42–12:12	ABS	Aldehyde/Ketones
	12	11:54–12:30	CO_2	Aldehyde/Ketones
June 30, 2020	13	10:17–12:17	ABS	AMP, PZ, NH_3
	14	10:27–12:33	CO_2	AMP, PZ, NH_3
	15	12:24–12:54	ABS	Aldehyde/Ketones
	16	12:38–13:13	CO_2	Aldehyde/Ketones

The plant operated in a stable condition through the entire test period, as shown in Figures 2 and 3 with controlled flue gas flow at 59,000 Sm^3/h and CO_2 controlled at 5 vol%, dry using recycled product gas.

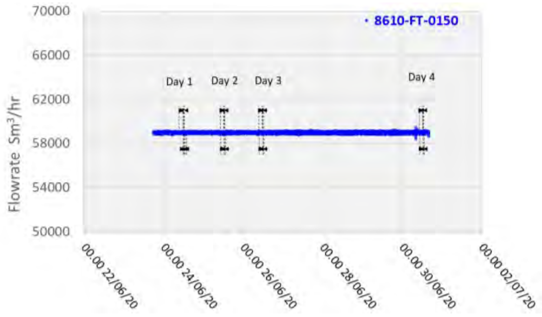

Figure 2**:** Flue gas flowrate through testing period

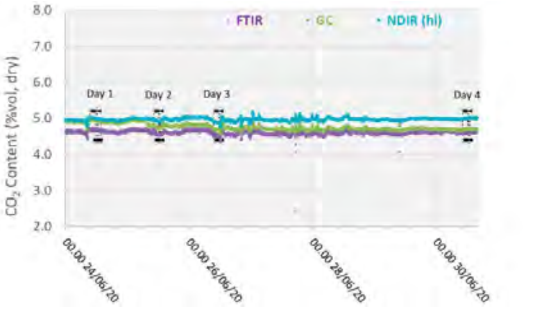

Figure 3**:** Inlet CO_2 concentration through testing period

3.1 CO_2 Capture Efficiency and Recovery

CO_2 capture efficiency can be quantified in several ways depending on how measurements have been taken and the expected accuracy of each individual measurement. Using different combinations of the measured parameters at the boundary of the process, four individual methods can be applied as detailed in Table 3.

These methods can rely on combinations of the available information to determine a capture efficiency, using the measured gas flowrates in combination with the CO_2 analyzer measurements.

Method 4 simplifies the measurement uncertainty by utilizing only CO_2 concentration data and making the well-founded assumption that all incoming inert gases (such as nitrogen and oxygen) will be unchanged through the absorption process. Hence, Method 4 can be used to compare against the other methods that utilize the flow measurements.

Table 3**:** CO_2 capture efficiency calculation methods

Method	Formula
1	$Efficiency = \frac{CO_2(\text{product})}{CO_2(\text{supply})}$
2	$Efficiency = \frac{CO_2(\text{product})}{CO_2(\text{product}) + CO_2(\text{depleted})}$
3	$Efficiency = \frac{CO_2(\text{supply}) - CO_2(\text{depleted})}{CO_2(\text{supply})}$
4	$Efficiency = 1 - \frac{O_{CO_2}}{(1 - O_{CO_2})} \frac{(1 - I_{CO_2})}{I_{CO_2}}$

The "CO_2 recovery" calculation is defined as the ratio of the sum of the CO_2 flow in depleted flue gas and the product CO_2 flow divided by the CO_2 flow in the flue gas supply.

$$Recovery = \frac{CO_2(\text{depleted}) + CO_2(\text{product})}{CO_2(supply)}$$

The CO_2 recovery is a measure of the closure of the CO_2 mass balance, being the fraction of CO_2 mass flow in the flue gas supply that is accounted for by measured CO_2 mass flows in the depleted flue gas and product CO_2.

Table 4 shows the four calculation methods of CO_2 capture and recovery for the test periods. Note that CO_2 product flow can be based on either the measured CO_2 product flow or by using the difference between the non-dispersive infrared-measured CO_2 supply and depleted flows. CO_2 capture rates calculated by all methods were in good agreement within each test period. It should be noted that Methods 3 and 4 are equivalent due to using the conserved oxygen and nitrogen method for outlet gas flow determination.

Table 4**:** CESAR-1 CHP sampling periods

#	Method 1, %	Method 2, %	Method 3, %	Method 4, %	Recovery %
1	96.70	97.85	97.88	97.88	98.80
2	97.77	97.85	97.86	97.86	99.92
3	97.43	97.91	97.92	97.92	99.50
4	97.35	98.03	98.05	98.05	99.29
5	97.28	97.95	97.96	97.96	99.30
6	97.23	97.95	97.97	97.97	99.24
7	96.99	97.90	97.91	97.91	99.05
8	97.28	97.87	97.89	97.89	99.38
9	97.57	98.23	98.25	98.25	99.31
10	97.61	98.25	98.26	98.26	99.34
11	98.94	98.37	98.36	98.36	100.6
12	98.31	98.47	98.47	98.47	99.84
13	97.06	98.84	98.87	98.87	98.17
14	96.80	98.81	98.84	98.84	97.94
15	96.77	98.72	98.75	98.75	98.00
16	96.84	98.73	98.76	98.76	98.05

Regardless of the method used, the CO_2 capture rate was consistently >96% as measured during all test periods. As the recovery rate was close to 100%, this implies consistency between the flue gas measurements and CO_2 concentration determination at all 3 locations.

3.2 Thermal Use

The reboiler heat duty or the heat released in the reboiler is calculated as the difference between steam enthalpy at reboiler inlet and the saturated water enthalpy at the reboiler condensate temperature. The specific thermal use (STU) is then calculated by dividing the reboiler heat duty by the product CO_2 flow.

$$STU_{product} = \frac{\dot{m}_{steam}(H_{steam} - H_{condensate})}{CO_2\ (product)}$$

$$STU_{captured} = \frac{\dot{m}_{steam}(H_{steam} - H_{condensate})}{CO_2\ (supply) - CO_2\ (depleted)}$$

The two corresponding values for specific thermal energy consumption are shown in Table 5 and were consistent during all test periods.

Table 5**:** Stripper reboiler specific thermal use

#	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

Prior testing at TCM using conventional 5M MEA solvent with CHP flue gas (3.5 vol% CO_2) at approximately an 80 tonnes-CO_2/day load yielded a regeneration energy range of 3.61–3.66 GJ/t-CO_2 using the product CO_2 flow and 3.58–3.60 GJ/t-CO_2 using the capture method, all carried out at 85% capture rate [3]. The CESAR-1 CHP tests (5 vol% CO_2) achieved circa 119 tonnes-CO_2/day load and achieved a regeneration energy range of 3.45–3.87 GJ/t-CO_2 using product flow and 3.41–3.89 GJ/t-CO_2 using the gas-side difference method.

It can be seen that the regeneration energy initially was near the bottom of the range for Tests 1 to 4 on June 24, and steadily increased in subsequent Tests 5 to 12. It was identified by TCM that excess foam formation in the stripper caused additional water condensation in the overhead stripper and an associated steam consumption increase. An antifoam agent was injected in the morning of June 30 by TCM operators with a subsequent rapid reduction in the regeneration energy measured in Tests 13 to 16, implying that the baseline CHP CESAR-1 regeneration energy is more in the range of 3.45–3.54 GJ/t-CO_2 using product flow and 3.41–3.48 GJ/t-CO_2 using the gas-side difference method when foaming is absent.

Importantly, the capture rate is 98% for these tests, far higher than the 85% capture rate for the MEA baseline tests, showing CESAR-1 solvent performs well at high capture rates as the regeneration energy is lower than MEA (when foaming was controlled) despite a capture rate of nearly 100%.

Recent testing at the Niederaussem pilot plant showed CESAR-1 solvent at 98% capture rate required only 3.22 GJ/tonne regeneration energy, however the inlet CO_2 concentration was 15.2% vol, dry as the flue gas source is from coal combustion [4]. Although the lower CO_2 concentration during these tests resulted in higher regeneration energy than observed at Niederaussem, some of the difference can also be attributed to the use of the RFCC stripper for these tests that is oversized for this regeneration load, operating at only 50% capacity. The CHP stripper was not used for these tests due to a combination of the 5% vol, dry inlet CO_2 concentration and the targeted 98% capture rate.

3.3 Process Contaminants

3.3.1 Aldehydes and Ketones

Formaldehyde, acetaldehyde, and acetone concentrations were determined by extractive sampling during the CESAR-1 CHP test periods. The data are shown in Table 6 for the depleted flue gas and in Table 7 for the CO_2 product.

Table 6**:** 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

The formaldehyde levels are lower than the previous MEA CHP baseline testing, which measured concentrations of 0.72 mg/Sm^3 by an external contractor. The acetaldehyde levels are also considerably lower with CESAR-1 than the MEA CHP test samples of 16 mg/Sm^3.

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 These species were also measured continuously with the Proton-Transfer-Reaction mass spectrometer (PTR-MS) that exhibits a very low detection limit capability (measuring in the ppb range). A sample of the data collected is shown in Figure 4, with higher formaldehyde levels (700–800 ppb) than measured by extractive samples (20–50 ppb), and comparable acetaldehyde and acetone measurements.

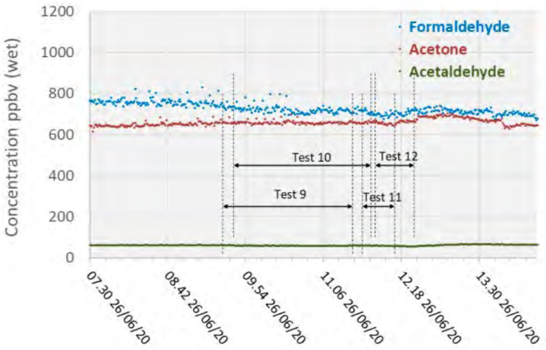

Figure 4**:** Depleted flue gas PTR-MS aldehyde and ketone measurements

For the CO_2 product, the formaldehyde levels detected were 2–4x higher than the manual-sampled measurements during the MEA CHP baseline campaign (0.14 mg/Sm^3) and the acetaldehyde levels were considerably lower than the previous level of 150 mg/Sm^3 measured for MEA.

Unlike the MEA tests, acetone was easily detected in the CO_2 product for CESAR-1, whereas in the previous MEA baseline all measurements taken were below the detection limit of 0.9 mg/Sm^3.

Table 7**:** Product CO_2 aldehyde/ketone concentrations

#	**Formaldehyde, mg/Sm^3**	**Acetaldehyde, mg/Sm^3**	**Acetone, mg/Sm^3**
2	0.63	0.93	21.7
8	0.42	0.61	23.1
10	0.39	0.57	28.5
16	0.18	0.27	16.7

The concentration of the depleted flue gas will be impacted by the CO_2 recycle stream, passing a portion of the contaminants shown back to the absorber inlet. With the exception of acetone, these components in the flue gas for the CESAR-1 testing were significantly lower than previous MEA measurements. This in turn suggests that these components are not significant degradation compounds from AMP and PZ, or that these solvents were not degraded to the same condition as for MEA.

3.3.2 Ammonia and Solvent Components

TCM measured concentrations of solvent components (AMP and PZ) along with ammonia during the CESAR-1 testing. Results of these manually extracted samples are shown in Table 8.

Table 8**:** 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

'<' denotes the limit of detection

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/Sm^3 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. 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.

With the exception of the first test, the AMP measurements were lower than the extractive samples. However, both strategies were likely near their method detection limits as levels were measured below 20 ppb in all cases. PZ was not detected by the PTR-MS instrument and hence was not included in Figure 5, however Acetonitrile was detected at 0.1 ppmv.

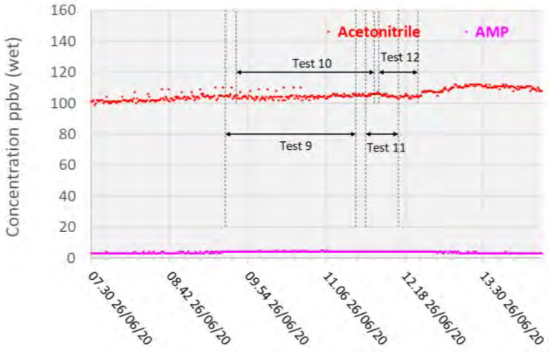

Figure 5**:** Depleted flue gas PTR-MS solvent measurements

Extractive solvent and ammonia samples were taken from the CO_2 product, and the results are shown in Table 9.

Table 9**:** Product CO_2 ammonia and solvent component concentrations

#	AMP, ppmvd	PZ, ppmvd	Ammonia, ppmvd
1	7.73	0.07	2.89
6	9.07	0.12	3.20
10	7.49	0.09	4.60
14	0.29	<0.007	3.59

'<' denotes the limit of detection

Similar to the depleted flue gas measurements, the AMP measurements were higher than the equivalent MEA samples, at 0.076 mg/Sm^3, and up to 2 orders of magnitude higher for AMP. PZ was detected in 3 of the 4 samples, but was present at very low concentrations.

Although ammonia desorption into the product gas is 2 orders of magnitude higher than the depleted flue gas levels, this is 4 times lower than the ammonia detected from the MEA CHP tests at 16 mg/Sm^3.

3.3.3 SO_2 and NOx

The TCM Fourier-transform infrared units installed for the flue gas supply and the depleted flue gas were configured to measure SO_2, NO, and NO_2 concentrations. The reported data are shown in Figures 6 and 7.

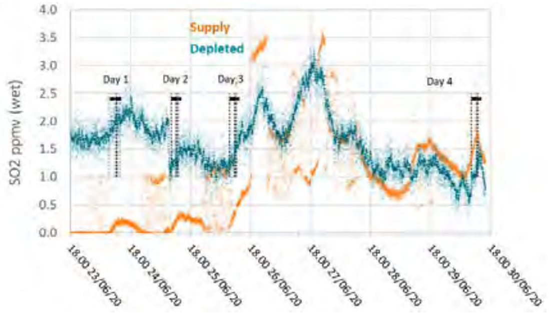

Figure 6**:** Supply and depleted flue gas SO_2 measurements throughout the test period

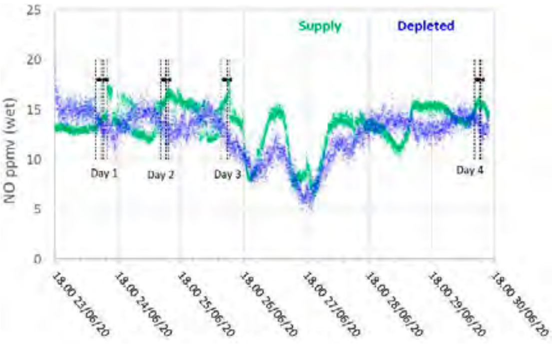

Figure 7**:** Supply and depleted flue gas NO measurements throughout the test period

During previous MEA testing, SO_2 levels leaving the absorber were consistently lower than the inlet measurement, likely due to absorption. This doesn't appear to be the case for CESAR-1 solvent, though the inconsistency in the incoming flue gas data doesn't allow a strong relationship to be established. Therefore, there was no way to determine SO_2 absorption rates for this solvent from the tests.

The NO data shows similar levels at the inlet and outlet, indicating minimal absorption into the CESAR-1 solvent. While absorbed NO_2 is known to contribute to the formation of nitrosamines in some solvents, the NO_2 data for the depleted gas were not recorded for these test periods. The average measured values in the flue gas for both NO and SO_2 leaving the absorber are shown in Table 10.

Table 10**:** Depleted flue gas SO_2 and NO concentrations

#	SO_2, ppmvd	NO, ppmvd
1	2.02	14.9
2	2.20	14.2
3	2.28	13.6
4	2.19	14.0
5	1.38	14.5
6	1.40	14.3
7	1.36	13.9
8	1.43	14.2
9	1.39	14.0
10	1.41	13.9
11	1.64	13.1
12	1.68	12.8
13	1.10	15.0
14	1.11	14.9
15	1.34	15.2
16	1.38	14.4

4. Conclusions

CESAR-1 solvent was tested at the TCM amine plant over 16 individual tests, during which extractive samples were taken, an overall summary of the tests is given in Table 11.

Table 11**:** Summary of CESAR-1 testing

Baseline Year	**2020**
Packing Height (m)	18
Flue Gas Flow (Sm^3/h)	59,000
Flue Gas Supply Temperature (°C)	38
Flue Gas Supply Pressure (bar)	0.02
Lean Amine Flow (kg/h)	58,000
Lean Loading	0.10
Rich Loading	0.52
Stripper Bottom Temperature (°C)	121
CO_2 Capture (%)	98
SRD (GJ/t-CO_2)	3.61

The plant was operated at 119 tonnes/day of CO_2 production with capture rates of 96–99%, exhibiting a near 100% mass balance.

Foaming was identified as causing stripper performance issues; however, when foaming was controlled, the regeneration energy for CESAR-1 solvent was 3.41–3.54 GJ/t-CO_2, lower than prior baseline testing of MEA at a lower capture rate of 85% at 3.58–3.66 GJ/t-CO_2.

Degradation products including formaldehyde, acetaldehyde and ammonia, were measured at lower levels for CESAR-1 solvent with acid water wash compared to results from MEA testing. As the solvent is a blend of AMP and PZ, both species were sampled showing higher levels of AMP than was measured for MEA and PZ being barely detectable due to the low vapor pressure of PZ.

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