AEROSOL EMISSION AT A POST COMBUSTION CO2 CAPTURE PLANT AT TWENCE (WTE FACILITY)

Juliana Monteiro [1*], Tanya Srivastava[1], Jasper Ros[1], Arjen Huizinga[1], Paul Gravesteijn[1], Peter van Os[1], Ronald de Vries[2], Mathijs Vos[2], Kirsten Telgenkamp[2], Susanna Sprauten Uhre[3], Hallvard Fjøsne Svendsen[3], Hanna K Knuutila[3]

[1] TNO, Leeghwaterstraat 46, 2628CA, Delft, The Netherlands

[2] Twence B.V., PO Box 870, Hengelo, 7550 AW, The Netherlands

[3] Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

* Corresponding author e-mail: juliana.monteiro@tno.nl

Abstract

Amine emissions in post combustion CO_2 capture (PCC) have a significant impact on process economics and the environment. The volatile nature of amine-based solvents in combination with aerosol formation can lead to amine emissions much higher than the design limit of PCCC plants. Aerosol management methods were implemented at the PCC pilot at Twence, a Waste-to-Energy plant in the east of The Netherlands. TNO carried out measurement campaigns at Twence with the aim to quantify amine emissions (both volatile and aerosol-based). The measurements indicated the necessity of implementing an aerosol mitigation technology, and a Brownian Demister Unit (BDU) was installed at the plant. The BDU removed more than 99% of the small particles (diameter below 5µm) from the flue gas, effectively controlling the MEA emissions at an average of 2.7 mg/Nm^3 at the pilot installation outlet.

Keywords: *CO_2 capture, aerosol-based emissions, solvent management, Brownian Demister Unit*

1. Introduction

Post-combustion CO_2 capture (PCC) is critical for reduction of greenhouse gas emissions, particularly in hard-to-decarbonize industrial sectors, such as Waste-to-Energy (WtE). Amine-based technology has been implemented for capturing CO_2 from several types of flue gas sources. CO_2 capture, using aqueous 30wt% monoethanolamine (MEA) is considered as the benchmark technology [1], and is also being used at pilot scale at Twence, a WtE plant located in the east of The Netherlands. Twence has formulated a multi year development roadmap based on three pillars: (1) Renewable energy generation, (2) Circular economy by closing energy and material loops and (3) Biobased economy by production of materials from biogenic waste streams. PCC can act as a bridging technology since it improves CO_2 footprint of CHP and can act as a building block molecule for production cycles. Thiis is represented in . Thus, Twence has been a first mover in accelerating WtE PCC.

Figure 1. Twence's CO_2 capture and utilization roadmap [2]

The CO_2 capture pilot used in this study was commissioned in 2014 [3], and has been operational since then. The pilot treats ca. 1.5 vol% of the flue gas from Twence's waste incinerator line (ca. 3300 Nm^3/h), and produces up to 500 kg/h of CO_2. Part of the CO_2 is used to produce sodium bicarbonate, which is in turn used in the flue gas de-sulfurization process. The remainder of the CO_2 is purified, liquified, and sold for external use (e.g., as food-grade CO_2 in the horticulture sector), see Figure 2.

Figure 2. Schematics of Twence's CO_2 capture pilot plant

There are economic and environmental challenges associated with the wide spread implementation of PCC. Emission of aqueous amine solvents, not only increases

the environmental impact of PCC, but also leads to higher operating costs. The volatile nature of amines contributes to emissions and observed MEA emissions in the treated flue gas at pilot plant operations are typically either below 10 mg/Nm^3 or in the range of 100–1500 mg/Nm^3 [4]. The high emission range is caused by aerosol-based emissions, and is significantly higher than the emission limit of 15 mg/Nm^3 proposed at the TCM plant [5]. Traditionally, water wash and demisters are used as emission management techniques. But these counter measures are not sufficient for mitigating aerosol-based amine emissions, which are caused by the presence of aerosol particles in the gas, with diameter below 5 µm [4]. The most mature technology (TRL7) for controlling aerosol-based amine emissions is the Brownian Demister Unit (BDU), a filter capable or removing small particles from the flue gas [4]. While the BDU was used at different campaigns at the TCM pilot plant, the publications on those campaign focus on reporting the efficiency in particle removal, but fail to report on the impact on amine emissions reduction [5], [6].

This work presents the use of an BDU at Twence to reduce aerosol emissions. It reports data measured by TNO during the CAMAK project in 2020 and 2021 (funded under the Dutch Topsector Energy program, project number DEI219004).

2. Aerosol Management

2.1 Measurement of aerosol-based emissions

In order to better understand and quantify amine emissions at the Twence pilot, measurement campaigns were carried out by TNO in April 2020. The emissions were measured using an Electrical Low Pressure Impactor (ELPI) for determination of particle size distributions and concentrations. Additionally, amine emissions were monitored using a Fourier Transform Infrared Spectrometer (FTIR). The ELPI was used for measurements at three different points in the plant, namely upstream the quench column, in between the quench and absorber columns, and downstream the water wash section of the absorber, as illustrated in Figure 3. This was done to understand the extent of formation of aerosols in the quench, and to correlate the observed emissions (FTIR data) with the particle number concentration (PNC, ELPI data).

ELPI emissions

In the measurements performed upstream the quench, the flue gas temperature was ca. 160ºC. The three measurements performed at this location are given in Figure 4, and are in relative good agreement. The average total PNC measured was 6.4 · 10^5 cm^{-3}. Approximately 90% of the particles were registered in the last impactor (D50% 6nm). Given the temperature at the sampling point, these particles are expected to be solid. While the three measurements can be interpreted as repetitions, variations in the sampling procedure were performed. In the first experiment ("normal"), the ELPI line was connected at the gas sampling port. In the second experiment, a probe was used. In the third experiment, a filter was placed in the ELPI line. While the differences registered are not significant, it is interesting to notice that the experiment with the filter allowed for registering particles throughout the measurement range (from 6nm to 5.44 µm), whereas for the other experiments, zero readings were recorded for some of the intermediate diameters. This measurement procedure is adopted in all measurements reported in this work from this point onwards. All measurements reported in Figure 4 were carried out on the 15th of April 2020.

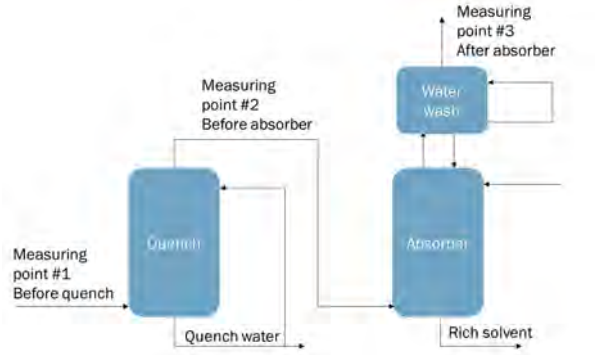

Figure 3 - Measurement points for the ELPI at Twence's capture pilot

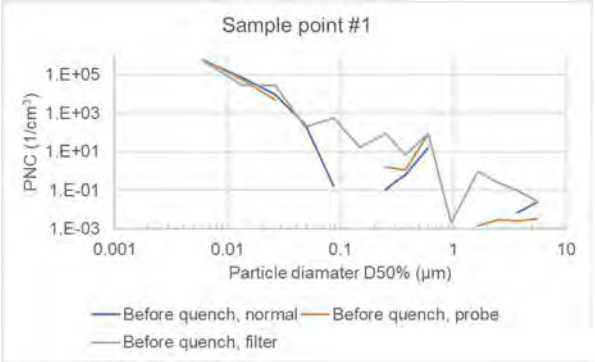

Figure 4 - Particle measurements in hot flue gas before quench, data from April 15th 2020

Measurements carried out downstream the quench (and upstream the absorber) were performed on the 7th and 15th of April 2020, and the observed PNC is given in Figure 5. The average total number of particles measured on the 7th was 3.4 · 10^7 cm^{-3}, while on the 15th it was significantly higher: 1.2 · 10^8 cm^{-3}. The reason for this variation is not known, and one hypothesis is that it is caused by variations in the WtE flue gas composition.

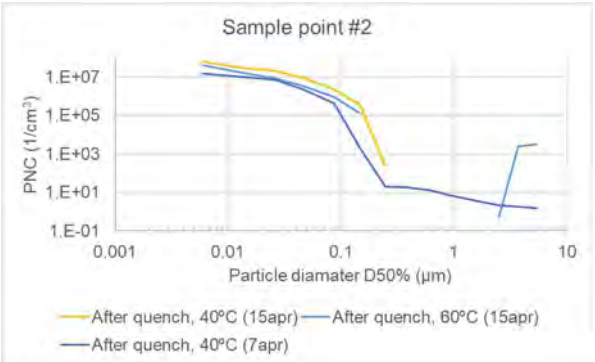

Figure 5 - Particle measurements before the absorber

The quench column is designed and operated to bring the temperature of the flue gas down from ca. 160ºC to ca. 40ºC. This is done by directly contacting cooling the gas with water. This leads to supersaturation of the gas phase, which contains acidic components such as HCl and SO_3. Nucleation in such environments is a well-known phenomenon in industrial wet scrubbing [7]. Both homogeneous and heterogeneous nucleation are possible in the Twence system, as foreign particles are present.

The total PNC measured at Twence after the quench is 2 orders of magniture higher than before the quench. While the particles measured downstream the quench mostly have diameter below 0.1 µm (see in Figure 5), the typical particle sizes of HCl aerosols is 1-3 µm, whereas H_2SO_4 leads to smaller particles, from 0.3-1.5 µm [7].

Measurements were also carried out after the absorber. An 80% decrease was observed in the total number of particles. The measured particles were approximately $7 \cdot 10^6$ cm^{-3}, while the PNC distribution shifted, as observed in Figure 6. This shift in the particle size distribution has an important effect: before the absorber, the total volume of the measured aerosols (considering perfect spheres) was $5.6 \cdot 10^{-10}$ cm^3/cm^3, whereas after the abosorber this increased to $1.4 \cdot 10^{-9}$ cm^3/cm^3.

The measured concentration of aerosol particles require that dedicated mitigation technologies are employed. A review of available technologies is given in [4]. For the Twence pilot plant case, it was decided to install a Brownian Demister Unit (BDU) downstream the quench column.

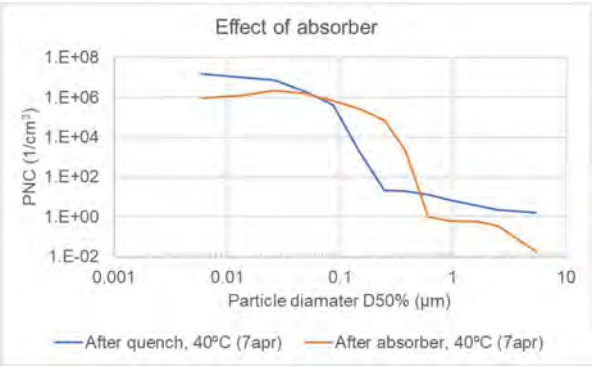

Figure 6 - Particle measurements after the absorber

FTIR measurements

The FTIR was used to measure MEA emissions at the absorber outlet (sample point #3). Emissions between 150 and 400 mg/Nm^3 were observed, as illustrated in Figure 7 (showing data for the 6th and 7th of april 2020). It should be noticed that the gas from the absorber outlet is mixed into the flue gas in the stack, and therefore the MEA concentration is diluted by ca. 70 times before it is emitted to the atmosphere. Therefore, the MEA emissions to the atmosphere, when the emissions at the pilot plant was at a peak value of 400 mg/Nm^3, was ca. 6 mg/Nm^3, which is in-line with emissions from other pilots and below the emission limit of 15 mg/Nm^3 proposed at the TCM plant [5]. As Twence doesn't have a specific emission limit for MEA this value is adopted in this study as a reference limit. Therefore, the emissions from the Twence pilot did not pose a risk to the environment or the plant operation. On the other hand, identifying the aerosol-based emissions at pilot scale allows for evaluating alternative mitigation solutions which can be implanted also at full scale (at Twence, but for amine-based PCC in general). These evaluations are described next.

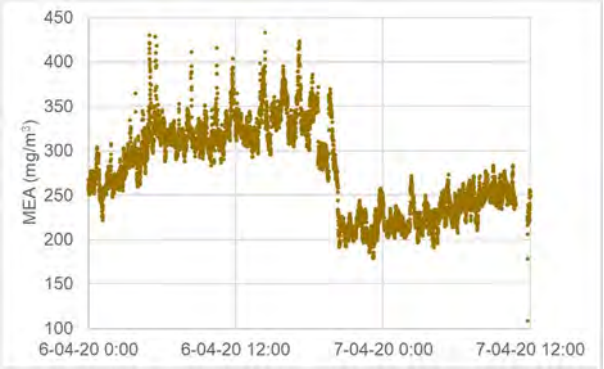

Figure 7 - MEA emissions at the absorber outlet, April 2020

2.2 Aerosol mitigation through plant operation

During the measurement campaign at the Twence pilot, operational parameters such as cooling in the quench and temperature of the lean solvent were varied. ELPI measurements were carried out at different operational settings to measure the impact of these strategies.

One mitigation strategy considered was to reduce the cooling in the quench to limit the degree of supersaturation, thereby limiting the increase in number of particles measured before the quench. During this test, the flue gas was cooled to 60°C, instead of 40ºC, which lead to a decrease in the PNC (see Figure 5), from $1.2 \cdot 10^8$ cm^{-3} to $7 \cdot 10^7$ cm^{-3}. While this is a relevant decrease, it is not enough to reduce the PNC to the point of mitigating aersol-based emissions, so this would not be an effective counter measure.

Another mitigation strategy explored was increasing the temperature of the lean solvent to accelerate the particle growth within the absorber. Measurements were carried out for lean solvent at 40°C and 50°C. However, the number of particles measured was similar for both cases ($9.9 \cdot 10^6$ and $1.2 \cdot 10^7$ respectively). Thus, this strategy also was deemed ineffective.

2.3 Use of Brownian Demister Unit (BDU)

Following the measurement campaign, it was concluded that additional mitigation strategies were required to enable further emissions management. A Brownian Demister Unit (BDU) was installed at the Twence pilot in March 2021 and TNO conducted a measurement to evaluate the efficiency of this emission mitigation technology.

The BDU is installed between the quench and the absorber columns. Therefore, the gas entering the BDU is saturated at 40ºC. The system is designed so that the BDU can easily be by-passed, to allow for tests with and without the BDU system inline ("BDU on/off").

A new series of ELPI measurements was performed on the 29th and 30th of March, 2021. The PNC was measured at the BDU inlet and outlet, as shown in Figure 8. The particle removal efficiency was above 99% throughout the measured particle diameter range. Two measurements were taken at the BDU inlet (1 and 2), one at the BDU outlet, and two at the water wash outlet (1 and 2), within an interval of 25 hours. During this interval, variations in the PNC were observed.

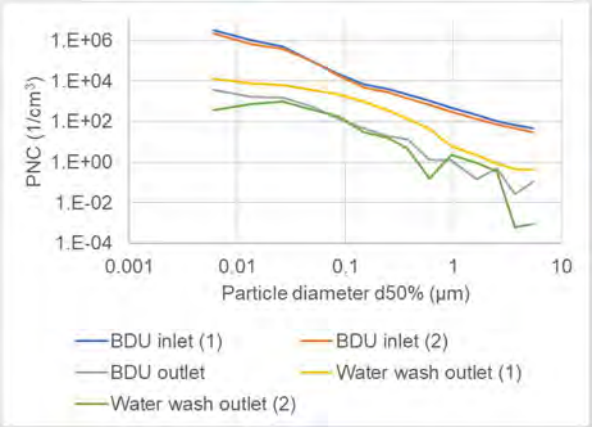

Figure 8 – Particle measurements around the BDU

The highest observed variation was in the water wash outlet (measuring point #3, see Figure 3). A long-term campaign is advised, to establish a correlation between the waste incinerator feeding process and the PNC.

The FTIR, connected downstream the absorber water wash, shows the effect on the MEA emissions. As made clear by Figure 9, the BDU has a clear effect of controlling the emissions. At stable operation with the BDU inline (BDU on), the MEA measurements averaged 2.7 mg/Nm^3, which is a low value and inline with measurements from other pilots [8], [9]. When the BDU was by-passed (BDU off), the emissions immediately increased, and averaged 750 mg/Nm^3 when stable. The dynamic response of switching the BDU "on" again is different then that of by-passing it, as can be observed in Figure 9. The measurements did not last long enough to determine how long it would take for the emissions would go back to the previous level.

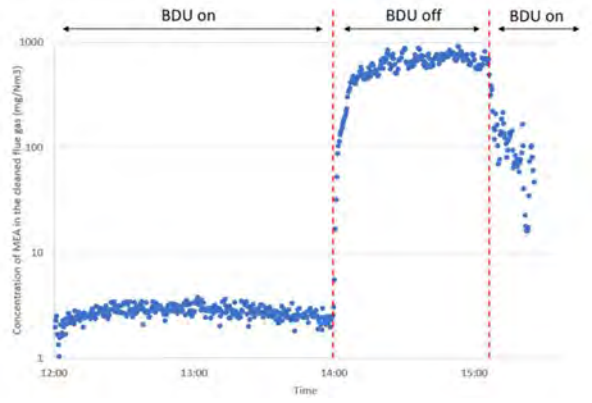

Figure 9 – MEA emissions at the pilot with and without the BDU

Again, it should be emphasized that the flue gas from the pilot is mixed with the stack flue gas before being emitted. The MEA emissions to the atmosphere, when the emissions at the pilot plant was at a peak value of 750 mg/Nm^3, are estimated at ca. 11.3 mg/Nm^3, below the reference limit of 15 mg/Nm^3.

2.4 Aerosol modelling

An aerosol model was used to simulate selected experimental cases to predict the chemical composition of the aerosol droplets and gain insight into the experimental results. Details of the model can be found elsewhere [10]–[12]. Based on an inlet droplet size distribution, the model predicts droplet growth and how the composition change throughout the absorber and water wash sections. A demister model was included showing the effect of a demister.

The model inputs are the flow rate, composition and temperature of the gas phase, the inlet droplet composition, number concentration and size distribution, and finally, a simulation showing the bulk liquid phase compositions and temperatures as a function of position in the absorber and water washes. These simulations were run using the simulation tool CO2SIM. A selected experimental run at the Twence capture plant was simulated. Both the absorber (height of 6 meters with the packing type Flexipac 250X), and water wash section of 1 meter were simulated. In the simulations, a demister is placed after the water wash. The agreement between the experimental rich loading, gas outlet temperature, and temperature profile in the absorber and simulation results was good, the main difference being the temperature profile in the absorber. The simulated temperatures in the absorber were compared to the experimental values.

Three aerosol cases were simulated. The number concentration of droplets entering the absorber was increased to see the effect on the emissions. As the presence of sulfuric acid can have a large impact on the emissions as it can act as nuclei in the aerosol formation and as the concentration of H_2SO_4 in nuclei entering the absorber was unknown, the effect of H_2SO_4 was studied by changing the concentration of sulfuric acid in the absorber inlet. An overview of the results is shown in Table 1.

Figure 10 shows the outlet droplet diameters in the absorber and water wash. The droplets grow heavily in the water wash at the same time as the MEA concentration in the droplets drops sharply. As the demister removes the largest droplets with the biggest impact on emissions, the emissions after the demister are significantly lower for all three cases (see Table 1). Table 1 also shows that increasing the number concentration will result in a higher MEA emissions due to larger interfacial area and droplet volume. Higher inlet H_2SO_4 concentration gives higher emissions of MEA. The baseline MEA emissions predicted by the model are in acceptable agreement with the measurements performed at the Twence pilot plant. Figure 11 shows a comparison

of outlet droplet size distribution compared with experimental data for Cases 1 and 2.

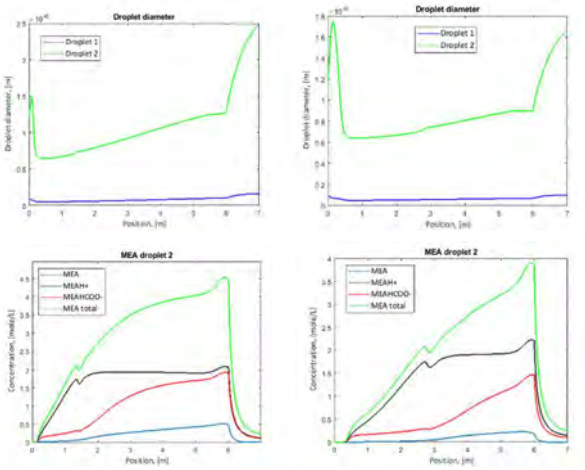

Figure 10 – Diameter of the droplets and MEA concentration as a function of position in the absorber (0-6 meters) and water wash (6-7 meters). On the left-hand side Case 1 and on the right-hand side Case 2.

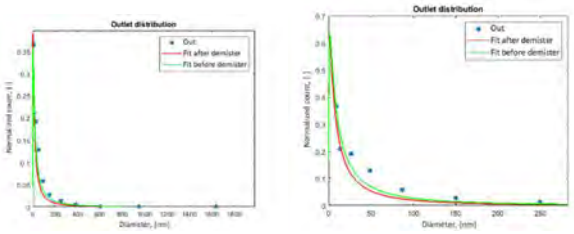

Figure 11 – Outlet distribution of droplets compared to experimental data. On the left-hand side Case 1 and on the right-hand side Case 2.

Table 1 – Summary of the modelling results

	Case 1	Case 2	Case 3
Droplets at the absorber inlet (droplets/cm^3)	$11.7 \cdot 10^6$	$50 \cdot 10^6$	$50 \cdot 10^6$
P_{H2O} at absorber inlet (kPa)	5.7	5.7	5.0
Inlet H_2SO_4 concentration (mol/L)	0.1	0.1	0.02
MEA after absorber (ppmv)	371	482	410
MEA before demister after water wash (ppmv)	135	189	142
MEA after demister (ppmv)	57	104	80
Droplets after demister (droplets/cm^3)	$11.6 \cdot 10^6$	$49.83 \cdot 10^6$	$49.86 \cdot 10^6$

4. Conclusions

Amine emission due to aerosol formation pose a risk to PCC plants right to operate. For large scale implementation of PCC, it is important to both understand and know how to control these emissions.

The measurement campaign at the Twence pilot illustrated the need for an additional mitigation strategy to counter aerosol-based amine emissions, theby improving economic and environmental performance. A BDU was installed and an experimental campaign was carried out to measure its impact. The measurements show that the BDU was able to remove more than 99% of the particles in the ELPI detection range. As a result, the MEA emissions are controlled at around 2.7 mg/Nm^3.

A model was used to predict aerosol-based emissions, with acceptable agreement with the measurements performed on-site. The results of the performed research are appropriate within the multi year development roadmap of Twence and add to PCC for WtE knowledge development.

Acknowledgements

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