Study of CO_2 Capture Solvent Emissions at the National Carbon Capture Center

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Abstract

To quantify emissions of amine-based CO_2 capture solvents, sampling of amine and ammonia emissions using a Fourier Transform Infrared (FTIR) spectrometer and a Phase Doppler Interferometer (PDI) was performed on the Slipstream Solvent Test Unit (SSTU) at the National Carbon Capture Center (NCCC) in October 2016. The amine and ammonia emissions rates were monitored at the water wash outlet under a variety of process conditions, and the results were compared to a previous sampling campaign performed in December 2015. It was found that treating the generating station's flue gas with a baghouse particulate removal unit reduced the amine emissions rate by an order of magnitude. This is due in part to the removal of fly ash aerosol nuclei from the flue gas stream. Aerosol drops were not observed by the PDI at the sampling location downstream of the water wash, indicating that amine aerosol from the SSTU were low in concentration and below the 0.1 μm detection limit of the PDI. Ammonia emissions were found to increase as the SSTU total run time increased, due to degradation of the amine solvent. Increasing the water wash gas outlet temperature correlated with an increase in the ammonia emissions rate. The amine emissions rate at the water wash outlet was found to be heavily dependent on the water wash gas outlet temperature, which was subsequently dependent on the water wash liquid temperature. A reduction in the water wash liquid temperature will reduce the water wash outlet gas temperature and subsequently reduce the amine and ammonia emissions rates.

Experimental Methods

Fourier Transform Infrared Spectrometry

FTIR spectrometry utilizes a broadband light source cast through a configuration of mirrors to measure how a sample absorbs light. Only infrared active compounds, such as CO_2, H_2O, and amines, will be detected by a FTIR. The mirrors in the FTIR are susceptible to damage from liquids, so the FTIR sampling is performed "hot and wet" throughout by maintaining a temperature of 180°C across the sampling system. All heated equipment is controlled by proportional–integral–derivative (PID) controllers using DC-pulse controlled solid-state relays. Power and thermocouple connections are made using cup-soldered female 7-pin Hirschmann^{TM} connectors, 4-pin Amphenol connectors, and K-type thermocouple junctions. A consequence of this "hot and wet" approach is a nondiscriminatory analysis of both liquids and vapors; the FTIR cannot differentiate between sampled liquids and gases. The FTIR is a useful instrument for obtaining overall emissions levels but requires coupling with an aerosol separation or characterization device to obtain data on gas phase or liquid phase compositions.

Table 1 shows the wavenumber (reciprocal wavelength) ranges used to quantify total emissions in this work. The number of references column refers to the quantity of background reference samples that were used for the component. FTIR reference spectra were generated with a Gasmet^{TM} Calibrator from Air Quality Analytical, Inc. The calibrator uses a needle valve and Aalborg mass flow controller (Model # GFM 17) to control the N_2 ballast gas flow rate. A Cole Parmer syringe pump (Model No 780100C) controls the injection of the calibration fluid from a 25-500 µL Hamilton® syringe. The calibration fluid is injected into a heated vaporization oven and passed to the FTIR inlet through a heated line at 180 °C. Table 1 shows the wavenumber (reciprocal wavelength) ranges used to quantify total emissions.

Table 1: Analysis regions used for FTIR spectra analysis

Component	Concentration	Range 1 [cm^{-1}]	Range 2 [cm^{-1}]	Range 3 [cm^{-1}]	# of References
H_2O	vol %	2475–2600	3000–3375	--	8
CO_2	vol %	926–1150	2065 - 2245	2550–2700	10
MEA	ppmv	895–1380	1810–2223	2550–3450	13
NH_3	ppmv	895–1300	2475–2600	--	7
SO_2	ppmv	1050–1450	2500–2600	--	7

Phase Doppler Interferometry

The PDI is an optical measurement device that quantifies the particle size distribution and number density for aerosol. Aerosol drops in the sampled stream are passed through intersecting lasers. A pair of photodetectors are used to observe the phase shift of light scattered as a droplet passes through the beam intersection. A third photodetector is used to provide redundant measurements and improve the resolution for smaller particles. The PDI operates by using the wavelength of light itself as the measurement scale instead of attempting to quantify light scattering, which reduces interference from window attenuation. By quantifying the phase shift induced by the beams refracting in the droplet, the droplet diameter can be calculated. The movement of the particle causes a Doppler shift in the frequency of light scattering, which allows the determination of the droplet velocity. By combining the velocity of the droplets with the number of droplets detected in a given time span, the particulate concentration and size distribution can be obtained. The PDI is capable of observing aerosol between 0.1 and 12.0 µm in diameter and at concentrations up to 10E7 per cm^3.

The PDI instrument itself is built by Artium Technologies, Inc., and consists of a transmitter, receiver, and data processing box. The transmitter and receiver are in a combined unit designed to fit around a specially sized spool piece, called the sample cell. The sample cell contains two “windows” for the lasers and an elaborate nitrogen purge system to keep the windows free of condensation.

FTIR and PDI Sampling at the National Carbon Capture Center

FTIR and PDI sampling was performed on the NCCC's SSTU during the first two weeks of October 2016. The NCCC is located in Wilsonville, Alabama, and utilizes flue gas from the Alabama Power E.C. Gaston Plant Unit 5, an 880 MW supercritical pulverized coal generation plant. The sampling location was at the outlet of the water wash column. The configuration of the SSTU process and the sampling system is presented in Figure 1.

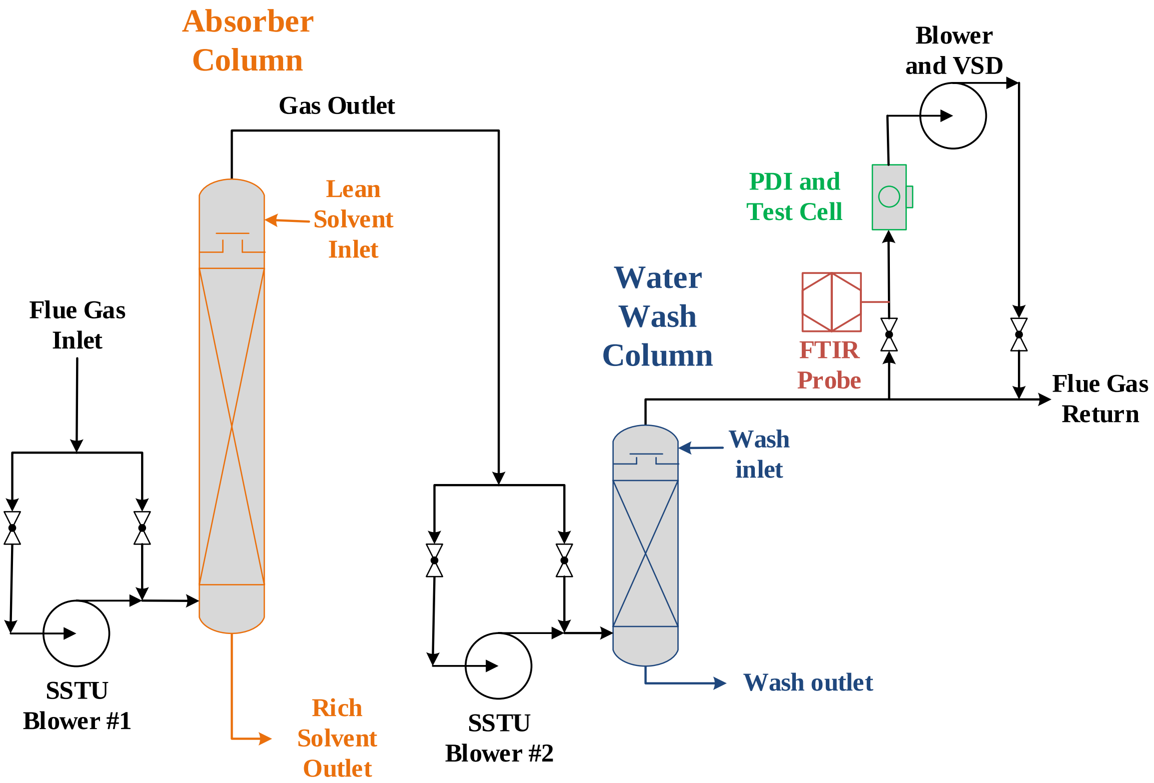

Figure 1: Process flow diagram of SSTU with FTIR and PDI sampling

The sampled stream was extracted via a VSD-controlled blower through a 4" sample valve that occupies approximately 30" of lateral length. The FTIR extracts a portion of the sample at this point for analysis of H_2O, CO_2, monoethanol amine (MEA) and NH_3 content. The remainder of the sample is passed through the PDI test cell for optical aerosol analysis. From the test cell, the sampled gas is suctioned through the blower and is then returned to the process stream.

The gas from the water wash outlet travels approximately 55' before reaching the sample port, and goes through a total of eleven 90° bends. Given a gas velocity of approximately 12 feet per second, this gives a residence time of 4.6 seconds. This may result in changes to the aerosol sizes and concentration density, due to potential convective cooling along the extensive piping length.

The SSTU does not have an existing FTIR sampling system, so a portable unit was transported to the site. The portable FTIR was a Gasmet DX4000 with a 9.8 meter path length and 4 cm^{-1} resolution. Background scans were performed every 24 hours to ensure a reliable background baseline for sampling.

Results

Impact of Baghouse on Aerosol Emissions

FTIR and PDI sampling was initially performed on the SSTU in December of 2015. Amine emissions were found to be over an order of magnitude higher than could be explained by volatility losses. The process configuration and operating conditions ruled out entrainment losses of amine solvent. Operation of the water wash column should effectively eliminate amine vapor emissions. Therefore, most of the amine measured resulted from aerosol phase emissions.

A baghouse was brought online early in 2016 for treatment of all the flue gas for Gaston Unit 5. The baghouse operates by injecting activated carbon into the flue gas stream, which adsorbs mercury, arsenic, and other heavy metals. The bag filters in the baghouse collect the activated carbon, which forms a cake layer on the bags. This has the added benefit of collecting fly ash particulates, which can lead to aerosol formation if allowed to enter the amine scrubbing system.

The primary purpose of the October 2016 campaign was to determine the effectiveness of the baghouse at mitigating aerosol emissions. Figure 2 presents the MEA emissions at the SSTU water wash outlet before (12/12/2015) and after (10/10/16) the baghouse installation.

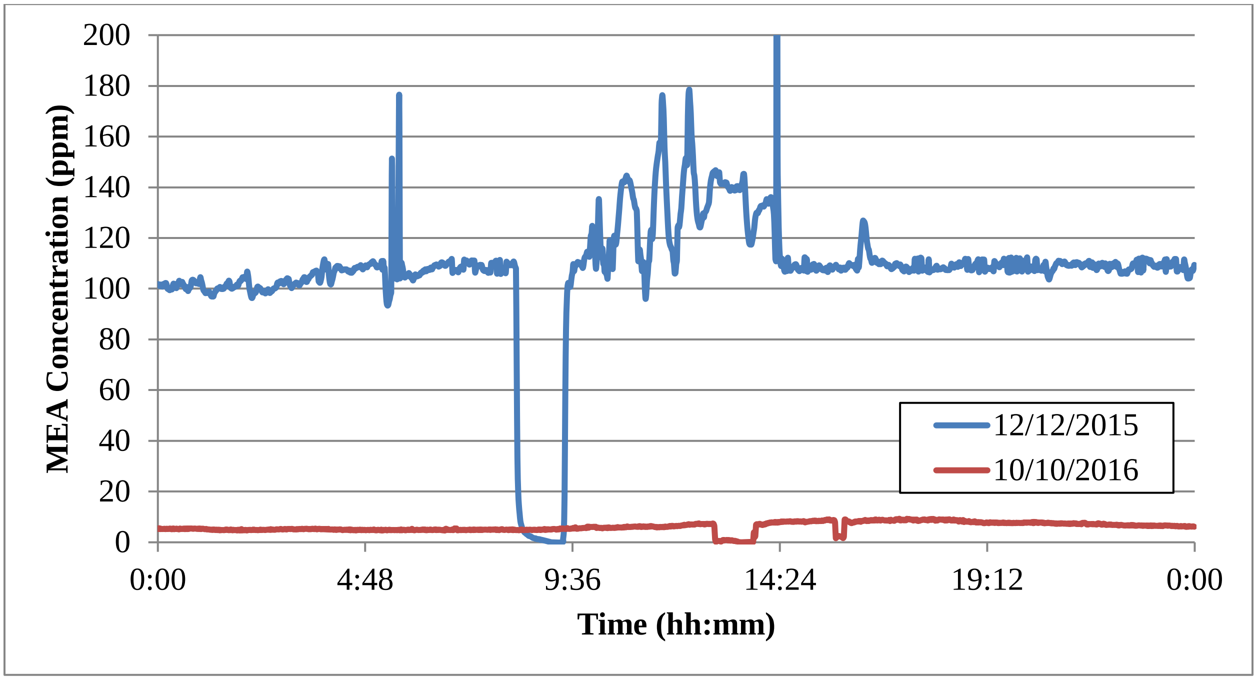

Figure 2: MEA emissions at water wash outlet, before and after baghouse installation

MEA emissions from the SSTU were between 100 and 110 ppm prior to the installation of the baghouse. These emissions rates were reduced to between 5 and 10 ppm after the baghouse startup. Similar operating conditions were maintained in the SSTU during both operating durations, indicating that the baghouse flue gas treatment step is responsible for a significant reduction in the amine emissions rate.

PDI Aerosol Measurements

The PDI was successfully utilized for aerosol characterization during the December 2015 sampling campaign. Aerosol drops as small as 0.1 μm were detected, with concentrations up to 10E7 per cm^3.

PDI sampling was again performed on the SSTU during the October 2016 campaign. During this sample run, no aerosols were observed despite continuous attempts to measure aerosols. The lack of aerosol observation was initially believed to be due to PDI instrument malfunction or user error. Diagnostic tests and troubleshooting results showed that the PDI was operating properly and that any aerosol emissions from the process were smaller than 0.1 μm in diameter.

The low outlet MEA concentration is the primary indicator of a reduced aerosol emissions rate. If a large concentration (>10E6) of aerosol nuclei are present in the amine scrubbing process inlet flue gas stream, MEA emissions will be greater than predicted by volatility alone.

As previously noted, the PDI operates by passing aerosol drops through intersecting laser beams. The PDI test cell is equipped with an observational window for manual confirmation of operation. An estimation of the aerosol concentration can be made by observing the intensity of the lasers; bright lasers indicate a high concentration of aerosol, while faint lasers indicate a low concentration of aerosol in the sampled stream. Figure 3 presents the PDI laser intersection as viewed in December 2015, while Figure 4 shows the same beam crossing in October 2016.

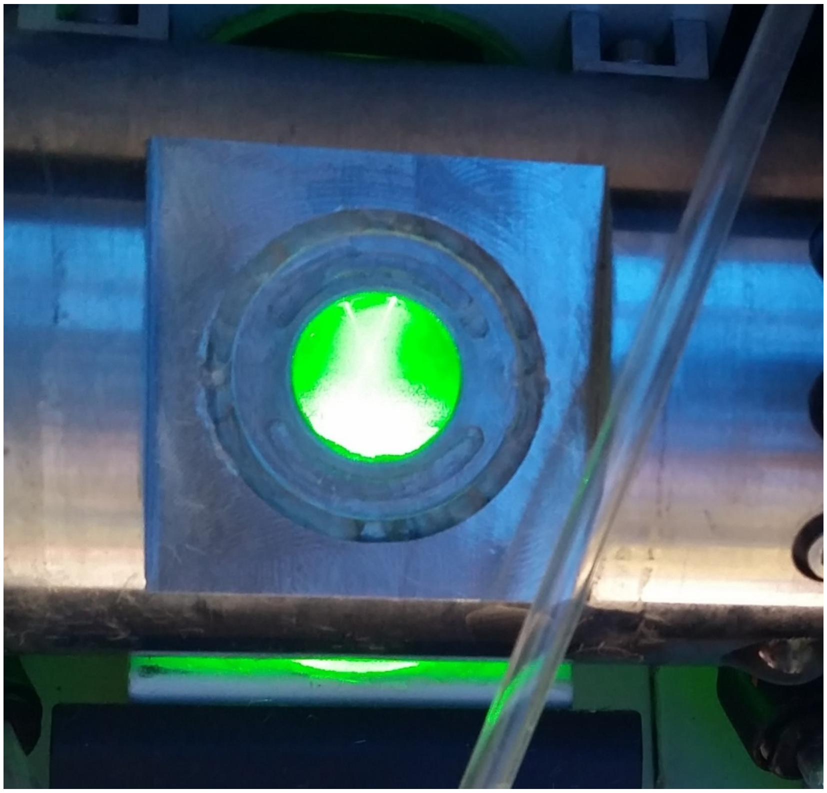

Figure 3: PDI laser intersection from December 2015

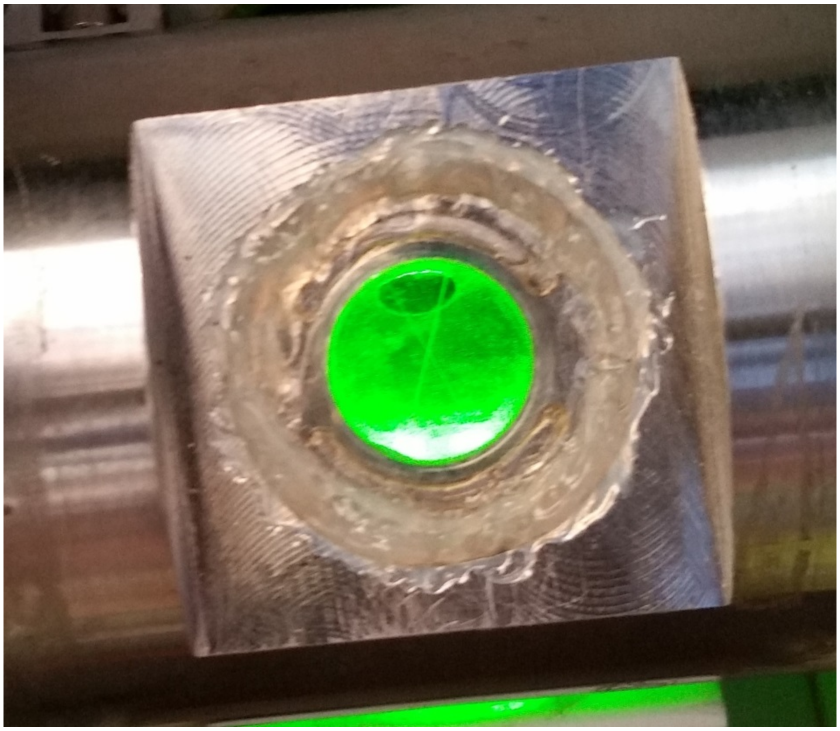

Figure 4: PDI laser intersection from October 2016

The laser intensity is significantly reduced from December 2015 to October 2016, due to a reduction in aerosol concentration and size. Although the lasers were still visible during the October 2016 tests, the PDI did not detect any aerosol, indicating that aerosol in the sampled stream were smaller than the lower bound of detection of 0.1 μm for the PDI.

The PDI is calibrated by the use of an oscilloscope. The oscilloscope is used to observe the three unprocessed photodetector signals; symmetrical Doppler burst Gaussian signals indicate the passage of a drop through a beam path. A forth signal is used as an indicator of a drop passing through the intersecting laser beams. Signal activity observed on the oscilloscope is a clear indication of the presence of measureable aerosol. Figure 5 presents an oscilloscope readout from December 5, 2015, while Figure 6 presents an oscilloscope display from October 10, 2016.

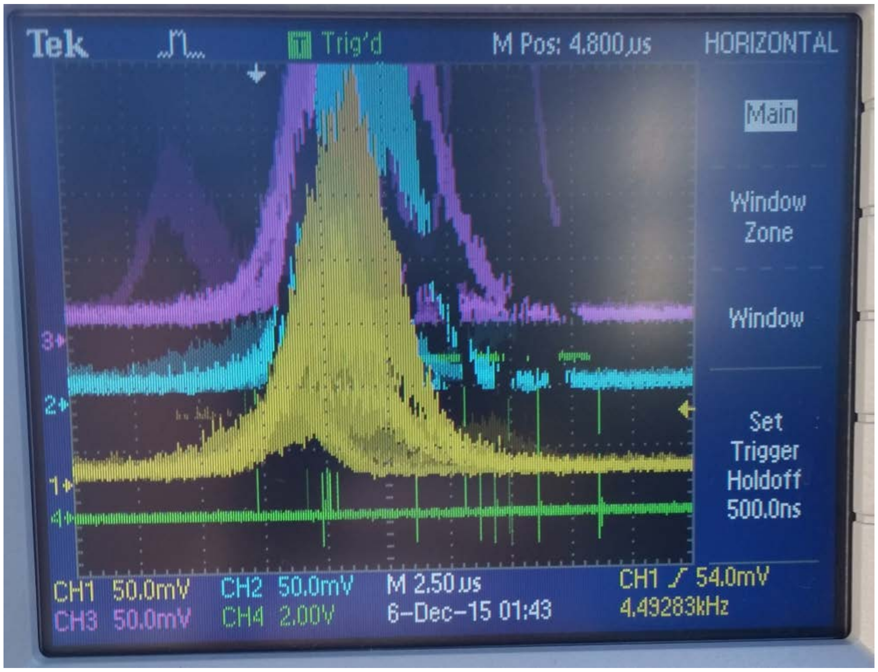

Figure 5: Oscilloscope display from 12/5/15

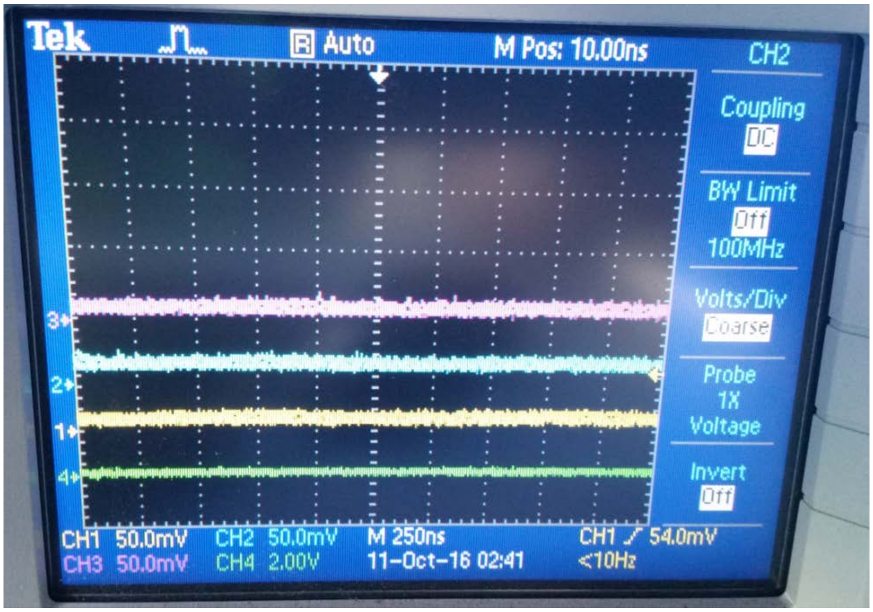

Figure 6: Oscilloscope display from 10/10/16

In Figure 5, the purple, blue, and yellow signals all display Gaussian Doppler bursts, indicating the presence of aerosol drops. The spikes in the green signal indicate the passage of a drop through the beam intersection. Despite identical voltage and range settings, the oscilloscope readout in Figure 6 shows no Doppler bursts from the photodetector signals. This further confirms the absence of aerosol drops at sizes greater than 0.1 μm.

Ammonia Emissions

Ammonia emissions at the SSTU water wash outlet were measured by FTIR throughout the October 2016 sampling campaign. The presence of NH_3 in the outlet stream from an amine scrubbing unit indicates the occurrence of amine degradation. Figure 7 presents the amine degradation in the SSTU over a six day period. The time range for the presented data is midnight until 9:00 AM each day, since minimal operational changes occurred during this time. The solid lines represent the ammonia concentration at the water wash outlet, given in ppm and scaled to the left y-axis. The dashed lines represent the temperature of the gas stream exiting the water wash column, and are scaled to the right y-axis.

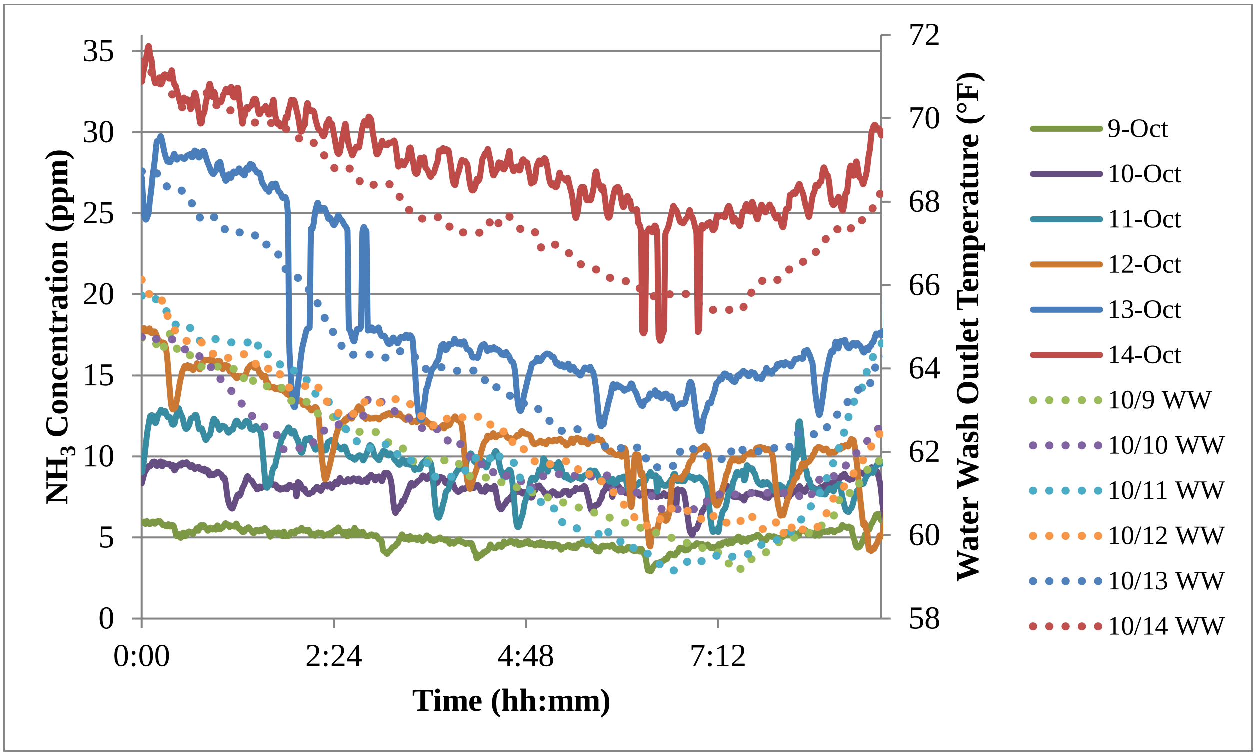

Figure 7: Ammonia emissions from SSTU, 10/9/2016 to 10/14/2016

Ammonia emissions are observed to increase as the water wash outlet temperature increases. From 10/9 until 10/12, the water wash outlet temperature remains relatively consistent. The ammonia emissions increase each successive day in this series, indicating that amine degradation is occurring. Ambient weather conditions are credited with the temperature variations observed. Over the last two days of sampling, the water wash outlet temperature increases from the temperature of the previous four days, due to increasing ambient temperatures. This results in further increases in ammonia emissions in addition to the daily increase in the ammonia emission rate. Amine degradation in the process results in an increase in ammonia emissions each successive day of operation, but operating the water wash at a lower temperature can help mitigate the ammonia emissions rate.

Effect of water wash temperature on MEA emissions

The relationship between the water wash outlet temperature, water wash liquid temperature, and MEA emissions rate was also observed. This is presented in Figure 8.

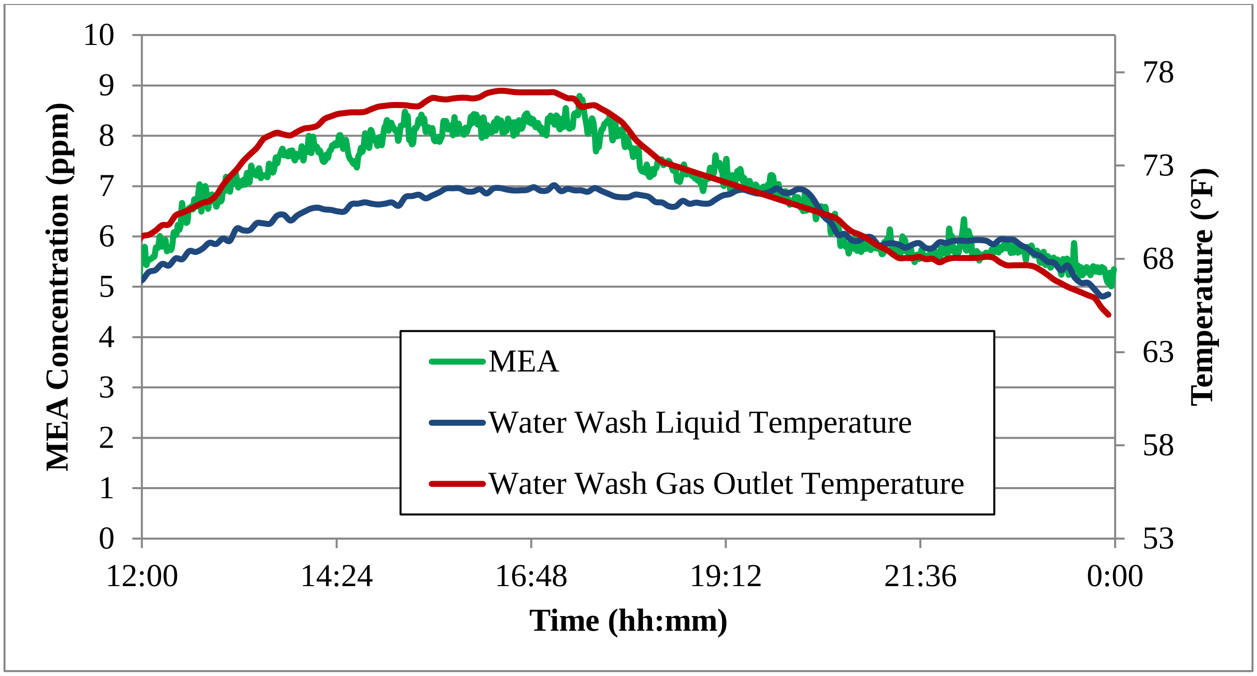

Figure 8: MEA emissions at water wash outlet as affected by water wash liquid temperature and water wash gas outlet temperature

The MEA emissions rate at the water wash outlet was observed to be slightly more dependent on the gas outlet temperature than the water wash liquid temperature. The amine emissions rate still correlates well with the liquid temperature due to the dependence of the gas outlet temperature on the liquid temperature within the water wash. Reducing the water wash liquid temperature will decrease the gas outlet temperature, resulting in a reduction in amine emissions.

Conclusions

The amine and ammonia emissions rates downstream of the SSTU water wash were monitored under a variety of process conditions. Treating the inlet flue gas with a baghouse particulate removal unit greatly reduced the amine emissions rate. Aerosol droplets were not detected by the PDI, indicating that aerosol were low in concentration and below the PDI's 0.1 μm detection limit. Amine solvent degradation led to increases in ammonia concentration as the SSTU total run time increased. An increase in the water wash gas outlet temperature correlated with an increase in the ammonia emissions. The amine emissions rate at the water wash outlet was found to be heavily dependent on the water wash gas outlet temperature, which itself was dependent on the water wash liquid temperature. Reducing the water wash liquid temperature lowers the water wash outlet gas temperature, and by consequence, reduces the amine and ammonia emissions rates.