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Solvent degradation and emissions from a 0.7MWe Pilot CO$_2$ capture system with two-stage stripping

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Abstract

The UKy-CAER team successfully tested an advanced 0.7 MWe post-combustion CO$_2$ capture system on a coal-fired power plant using a heat integration process combined with two-stage stripping to enhance the CO$_2$ absorber performance. One of the unique feature of the UKy-CAER integrated process is a two-stage stripping unit for solvent regeneration. The secondary stripper is empowered by the heat rejection from a conventional steam-heated (primary) stripper. The secondary stripper outlet stream at the commercial scale can be used as boiler secondary combustion air, consequently enriching the flue gas with CO$_2$, resulting in less energy penalty required by the CO$_2$ capture system. The primary goal of this study was to form an initial assessment of the impact on the amine solvent from coal combustion flue gas contaminants and the potential higher oxygen content in the solvent due to incorporation of the secondary air stripper into the conventional amine scrubber/stripper system. The overall oxidative degradation was comparable to previous reports with 30 wt% MEA solvent at similar flue gas run hours. This suggests that the addition of the secondary air stripper appears to be negligible with regards to solvent oxidation.

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1. Introduction

Solvent degradation can be a major factor when evaluating the cost associated with carbon capture using aqueous amine solvents. One significant source of amine degradation is through reactions with flue gas components, specifically soluble acidic flue gases including SO_2, NO_x, and HCl, leading to the formation of heat stable salts (HSS) [1]. Amine oxidative degradation can also produce HSS species including acetate, formate, glycolate and oxalate. These degradation products can contribute to amine losses, impact system economics, create environmental impacts and contribute to additional solvent degradation [2]. Degradation product accumulation can also have a significant impact on process operations by increasing solvent viscosity, causing foaming in the absorber, and increasing the corrosion behavior of amine solvents in carbon capture operations.

Degradation not only reduces the concentration of free amines in solution, and subsequently the solvent CO_2 absorption capacity, degradation products can also cause environmental issues. Research into degradation of aqueous amines has focused on three key routes: oxidative degradation; formation of heat stable salts from flue gas components; and amine polymerization or thermal degradation. Oxidative degradation is the most rapid amine degradation route during PCC and is driven by both the reactivity of amines and the relatively high oxygen content in flue gas. Dissolved metals (from corrosion and fly ash intrusion) are also known to catalyze oxidative degradation in aqueous amines [3]. To better understand and prevent amine degradation in coal combustion flue gas capture units, it is crucial to identity all degradation products.

Emissions from amine-based carbon capture systems are also an area of significant concern. Analysis and monitoring of gas-phase emissions can contribute to the larger understanding of solvent degradation inside a coal combustion flue gas capture system. One key degradation product is ammonia, which is formed through oxidative degradation of many aqueous amine solvents. Amines are also present in the gas-phase as entrained droplets, aerosols and to a lesser extent as volatile amine, due to their relatively low vapor pressure.

The UKy-CAER team operates an advanced 0.7 MWe post-combustion CO_2 capture system on a coal-fired power plant using a heat integration process combined with two-stage stripping to enhance the CO_2 absorber performance. The integrated UKy-CAER technology work synergistically to achieve fast CO_2 absorption, with high CO_2 loadings and cyclic capacity which allows the solvent regeneration process to be performed at relative lower temperature to minimize solvent degradation. The unique features of the UKy-CAER process include heat integration, a two-stage cooling tower and an air driven secondary stripping unit for solvent regeneration inserted between a conventional rich-lean crossover heat exchanger and a lean solution temperature polishing heat exchanger. The secondary stripper is empowered by the heat rejection from a conventional steam-heated (primary) stripper. The secondary stripper outlet stream at the commercial scale can be used as boiler secondary combustion air, consequently enriching the flue gas with CO_2, resulting in less energy penalty required by the CO_2 capture system.

The secondary stripper air-flow has the potential to lead to higher rates of oxidative degradation of the aqueous amines, which can be evaluated by analyzing the formation of oxidative degradation compounds. The primary goal of this study was to form an initial assessment of the impact on the amine solvent from coal combustion flue gas contaminants and the potential higher oxygen content in the solvent due to incorporation of the secondary air stripper into the conventional amine scrubber/stripper system.

Nomenclature	
HPLC	High Pressure Liquid Chromatography
HSS	Heat stable salts
MWe	Megawatt electric

PCC	Post combustion capture
ppmV	Volumetric parts per million
UKy-CAER	University of Kentucky Center for Applied Energy Research

2. Experimental

2.1. UKy-CAER 0.7 MWe small pilot CO_2 capture unit

The UKy-CAER 0.7 MWe small pilot CO_2 capture facility is located at Kentucky Utilities E.W. Brown Generating Station in Harrodsburg, Kentucky. Coal combustion flue gas is extracted after a series of emission controls including low NOx, ESP and a wet flue gas desulfurization unit. A flow diagram of the UKy-CAER small pilot CO_2 capture facility is shown in Fig. 1, with general operating condition listed in Table 1. The capture unit includes a pretreatment tower using soda ash to reduce the SO_2 level in the flue gas to below 5 ppm before it enters the absorber column. The absorber has intercooling and an integrated emission reduction pad, but no standalone water wash column. The conventional stripper/reboiler regeneration unit is augmented with a secondary air stripper that further lowers the CO_2 content in the lean solvent before it returns to the absorber. The secondary stripper exit gas can be recycled as boiler combustion air at the commercial scale, resulting in a higher CO_2 content in the flue gas (14% vs 10%) which increases CO_2 mass transfer and rich solvent loading and results in lower regeneration energy. This process is replicated at the pilot scale using a slipstream of the product CO_2 that is recycled and doped into the flue gas before the pretreatment tower.
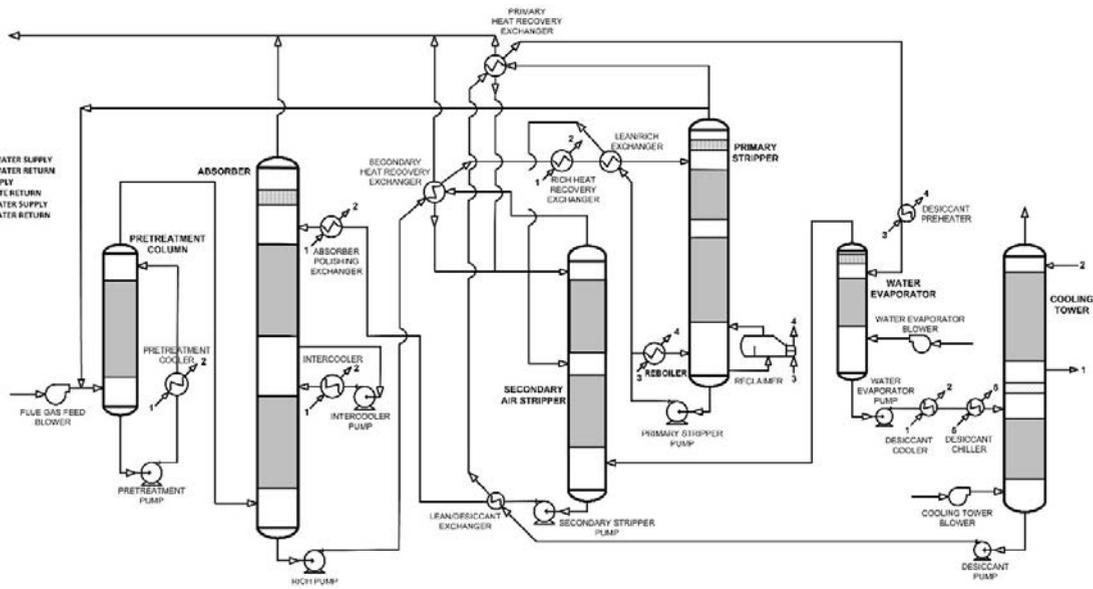

Fig. 1. Flow diagram of UKy-CAER 0.7 MWe small pilot CO_2 capture plant.

Table 1. General operating parameters of the UKy-CAER 0.7 MWe small pilot CO_2 capture plant during solvent testing.

[a]CO_2 (vol%)	O_2 (vol%)	SO_2 (ppm)	NO_x (ppm)	Lean Amine Temperature (°C)
14.0	8	< 5	< 50	100
[a] Achieved with doping from primary stripper CO_2 product gas.				

2.2. Monoethanolamine solvent testing

An initial change of 30% MEA, as a baseline solvent, was used in order to better understand the impact of the secondary air stripper on system performance and solvent degradation. Monoethanolamine (99%, Univar) was diluted with plant service water and maintained in the operational concentration range of 25-30% (4-5 mol/Kg alkalinity) with periodic amine make-up, but without the addition of any anti-oxidation or anti-corrosion additives. The full solvent testing period included the inceptive unit start-up and commissioning, parametric testing and long-term operation. For the first 870 hours, the solvent was not cleaned or purified. This was followed by a period of approximately 90 hours where the solvent was thermally reclaimed with a 20% soda ash caustic solution. After this period, the solvent was not cleaned or purified through the end of the testing campaign, totaling approximately 1320 operating hours. Operating hours refer only to periods when flue gas was contacting the solvent (CO_2 was being captured) and steam was used for regeneration.

In this study, HSS accumulation and MEA degradation products were monitored during parametric and long-term testing periods. Heavy metal accumulation, from flue gas constituents and material corrosion, was monitored from the beginning of the initial MEA solvent system charging through solvent reclaiming (0 - 870 operating hours). MEA and ammonia emissions were monitoring during the long-term testing period after reclaiming.

2.3. Solvent degradation

Detection and quantitation of anionic flue gas heat stable salts (HSS) and several MEA oxidative degradation products was performed with a Dionex ICS-3000 Ion Chromatography system (Dionex-ThermoScientific, Sunnyvale, CA) using an KOH eluent gradient described elsewhere [4]. Certified anion standards of chloride, nitrite, nitrate, sulfate, acetate, oxalate and formate were obtained from Environmental Express (Charleston, SC). A glycolate standard was obtained from Alltech (Deerfield IL). Individual calibration standards for each anion were prepared by diluting the standards with 18.2 MΩ water. Amine samples were prepared with 18.2 MΩ water to a 500x dilution factor. Each sample was analyzed in triplicate and reported as an average value.

MEA solvent samples were analyzed to identify and quantify additional oxidative and thermal degradation product with an Agilent HPLC coupled with a Time of Flight Mass Spectrometer (TOF-MS). The HPLC contained a Pinnacle DB AQ C18 10 x 2.1 mm guard column and a Pinnacle DB AQ C18, 50 x 3 mm, 3µm analytical column (Restek, Bellafonte PA). The mobile phase was a mixture of water with 0.01% formic acid (90%) and methanol (10%). Injection volume was 10µL and the flow rate was 0.3 mL/min. The TOF-MS was operated in duel electrospray ionization (ESI) positive mode with mass scan range of 30-1000 m/z. Calibrations standards of N-(2-hydroxyethyl)imidazolidin-2-one (HEIA, 75% in water), N-(2-hydroxyethyl) imidazole (HEI, 97%), and N-(2-hydroxyethyl)ethylenediamine (HEEDA, 99%) were purchased from Sigma-Aldrich (St. Louis, MO) and prepared in mobile phase from 0.01 – 50 mg/L. Amine samples were also prepared in the mobile phase to a 500 times dilution factor. Each sample was analyzed in triplicate and reported as an average value.

The concentrations of metal elements in the solvent was examined using acidic microwave digestion, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian), and ICP Mass Spectrometry (ICP-MS, Agilent). ICP-OES was used to analyze the initial solvent samples and ICP-MS was used for the last samples collected before reclaiming at 870 operating hours. Calibration standards were prepared from commercial stock solutions

(Environmental Express) in 1% nitric acid, ranging from 0.01 ppb to 50 ppm. The amine solvent samples were digested in an open vessel microwave manifold system and diluted to a final nitric acid concentration of 1%, which resulted in a total sample dilution factor of 25 times.

2.4. Gas sampling

A gas sampling port was installed at the absorber exit to monitor gas phase degradation products and amine emissions. Gas samples were collected using sampling methodology adapted from EPA Method 1, 5 and CTM-027. Briefly, samples were withdrawn from the flue gas duct through an impinger train containing a reagent solution. Gaseous ammonia and amines were collected in an aqueous 0.1N sulfuric acid (H_2SO_4) solution, which was then analyzed by ion chromatography.

3. Results and Discussion

The primary goal of this study was to understand the impact on the MEA solvent of flue gas constituents and the potential higher oxygen content in the solvent due to incorporation of the secondary air stripper. The secondary stripper air flow may lead to higher rates of oxidative degradation, which can be evaluated by analyzing the formation of oxidative degradation compounds in the solvent. Thermal reclaiming was conducted during a short period between 870-980 operating hours, as noted in the figures and represented by the lower analyte concentration levels in the solvent after reclaiming.

3.1. Heat stable salts

The accumulation of the flue gas HSS species is presented in Fig. 2, through a total of 1320 solvent run hours. As previously described in the experimental section, the SO_2 concentration in the flue gas entering the absorber was maintained at below 5 ppm by polishing with soda ash in the pretreatment tower. As expected, even with the additional SO_2 polishing, the major HSS species accumulating in the solvent was is sulfate. The high solubility of SO_2 in the MEA lead to a steady accumulation of sulfate in the solvent reaching a maximum of 3640 mg/L at 800 hours. Likewise, nitrate and chloride levels also showed steady accumulation rates, although at lower absolute concentrations. Nitrate ready a maximum of 1110 mg/L before reclaiming, while chloride reached a maximum concentration of 193 mg/L during the same period. The small drop in concentrations between 800 and 870 hours is due to dilution of the solvent from water accumulation during an extended period of system downtime. After reclaiming through the end of the testing campaign the chloride concentration remained unchanged, while the sulfate and nitrate returned to similar accumulation rates.

The formation of oxidative HSS species from MEA are presented in Fig. 3. The major oxidative HSS is formate, which was expected and is commonly used as an indication of overall oxidative degradation [3]. The total oxidative HSS reached close to 12670 mg/L or approximately 1.16 wt% before reclaiming. This number is equivalent to approximately 4% loss of the initial MEA loaded into the system (30% is equal to 300,000 mg/L). The overall oxidation in the form of HSS is comparable to previous reports with a straight (without anti-oxidation inhibitors) 30 wt% MEA solvent [5-7].
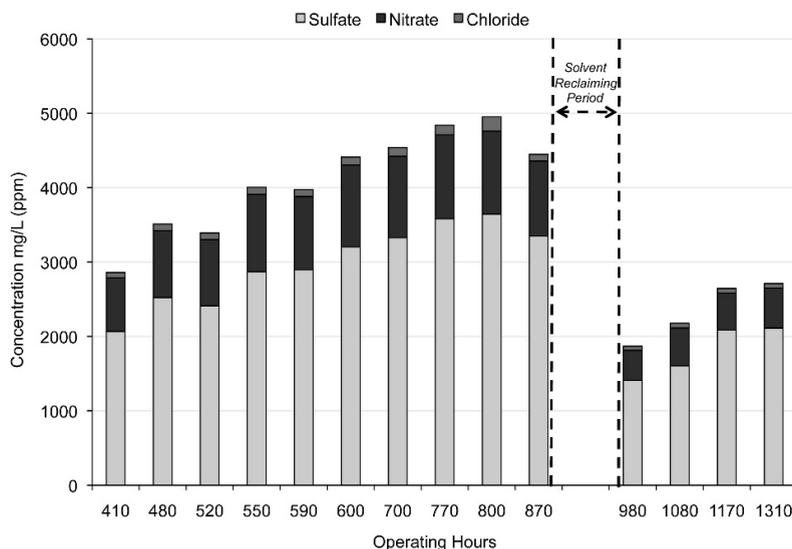
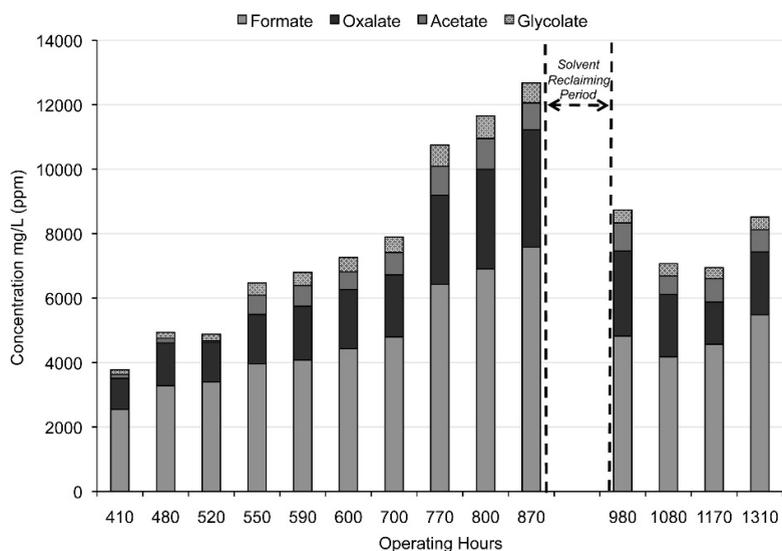Fig. 2. Flue gas HSS accumulation in MEA solvent during long-term testing.

Fig. 3. Oxidation degradation HSS formation in MEA solvent during long-term testing.

3.2. MEA degradation – polymerization

The accumulation rates of the major polymeric amine oxidative degradation compounds identified by TOF-MS are presented in Fig. 4. The main oxidative product identified in the MEA solvent was N-(2-hydroxyethyl)-1H-imidazole (HEI). HEI is very important molecular marker for oxidative degradation of MEA and is formed through a complex

mechanism, which is still not completely under-stood [5]. Due to the likely presence of several free radicals from oxidation, there could be several possible pathways to make HEI and the other major oxidative degradation compound identified, N-(2-hydroxyethyl)-2 methyl imidazole (HEMI) [8]. The second most abundant degradation compound is N-(2-hydroxyethyl)imidazolidin-2-one (HEIA), a commonly observed thermal degradation product [9]. N-[2-[(2-Hydroxyethyl)amino]ethyl]imidazolidin-2-one (HEAEIA) and N-(2-hydroxyethyl)ethylenediamine (HEEDA) were also observed in this MEA solvent, although at relatively low concentrations and later in the testing campaign as the solvent continued to degrade. The rate of the formation and accumulation of these containments are similar to other published MEA campaigns, at similar flue gas run hours [5,6]. This suggests that the addition of the secondary air stripper does not lead to a significant increase in solvent oxidation.
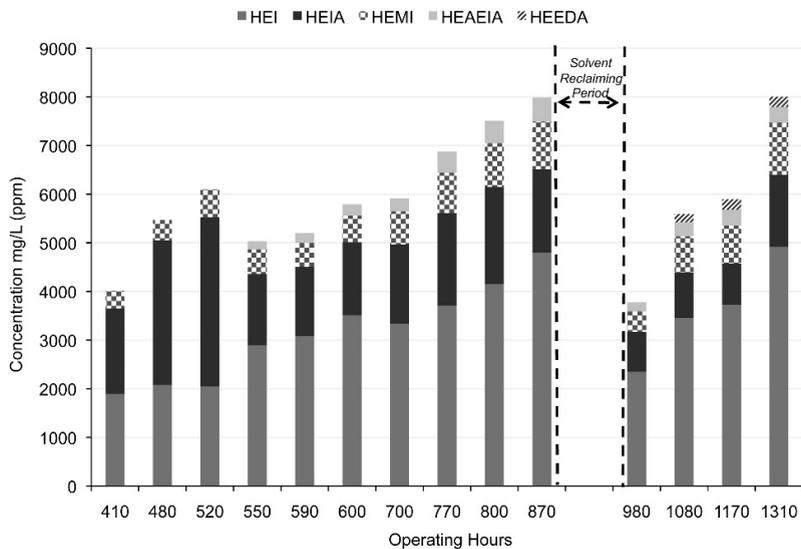

Fig. 4. MEA degradation through polymerization during long-term testing.

3.3. RCRA and corrosion metal accumulation

Metals and nonmetals can accumulate in process solvents from the introduction of coal-derived fly ash and by corrosion of structural components [10]. Although these elements typically accumulate at trace levels (ppb and ppm concentrations), they can be involved in reactions with amines that accelerate solvent degradation and corrosion [3,11]. These trace elements can also accumulation over the duration of the solvent testing campaign and potentially impact the cost and treatment of spent solvent disposal by exceeding non-RCRA hazardous waste characterization limits.

Eight of the ten elements monitored, the RCRA-8 minus mercury (Cr, As, Se, Ba, Pb, Ag, Cd) and additional steel corrosion metals (Fe, Ni, Cu) were detected in the MEA solvent over the duration of the campaign. Ag and Cd were not detected in the MEA solvent above the detection limit. Metal concentrations increased with continued operation until the solvent was reclaimed at 870 hours. The solvent concentrations and observed accumulation rates for the eight elements (before solvent reclaiming) are listed in Table 2.

The results for copper accumulation in the solvent were by far the most interesting from this analysis, with copper reaching a maximum of 33 ppm, a significantly higher concentration than was anticipated. Copper could be from fly

ash, but is more likely from corrosion of a yet unidentified amine loop component(s). Copper, along with iron, are metals that are reported to significantly accelerate amine oxidative degradation and produce higher ammonia levels [12]. The identification of the copper source(s) is a current point of investigation.

Iron was the most abundant metal observed in the MEA solvent, reaching a maximum of 265 ppm at 870 operating hours. Chromium rose to a maximum of 29.4 ppm, while nickel reached 28 ppm after 870 hours of operation. Iron, along with nickel and chromium, could be introduced to the solvent through steel corrosion, and to a lesser extent from coal fly ash. Lead reached a maximum of 3.65 ppm, but this amount is below the RCRA hazardous waste allowable limit of 5 ppm. Lead is a known component of coal and likely introduced via fly ash. Likewise, the barium concentration reached 0.98 ppm and stayed well below the RCRA hazardous waste level of 100 ppm. Both Selenium and Arsenic levels remained below the RCRA allowable levels of 5 ppm and 1ppm for hazardous waste, with final concentrations of 0.77 ppm and 0.29 ppm respectively.

With regards to waste solvent disposal, the chromium concentration exceeded the limit of 5 ppm for non-RCRA hazardous waste classification, meaning any spent solvent at this stage would be classified as RCRA hazardous waste for disposal. At this point in the testing campaign, the solvent was thermally reclaimed to reduce the concentration of metals and degradation products. Analysis of the effectiveness of thermal reclaiming in reducing the metal content in the solvent is currently ongoing.

Table 2. Heavy metal accumulation in MEA solvent during start-up, parametric and long term testing (before solvent reclaiming).

Analyte	Elemental concentration in MEA solvent before solvent reclaiming at 870 hr. (mg/L)	Accumulation rate from initial solvent charge through beginning of solvent reclaiming (mg L^{-1}/hr)
Fe	265	0.3014
Cr	29.4	0.0333
Cu	33.9	0.0385
Ni	28.0	0.0318
Pb	3.65	0.0042
Ba	0.98	0.0011
Se	0.77	0.0009
As	0.29	0.0003
Ag	< LOD[a]	-
Cd	<LOD[b]	-
[a] Limit of detection (LOD) for Ag = 0.625 mg/L; [b] LOD for Cd = 0.25 mg/L		

3.4. MEA and ammonia emissions

Ammonia and MEA emissions from the absorber exit are presented in Fig. 5. Multiple samples were collected on each sampling day to maximum the amount of emissions data collected. The first sample set, at approximately 960 hours was collected just before the solvent reclaiming period had ended, while the remaining samples were collected as the solvent was allowed to degrade. Ammonia emissions range from 56 ppmV to 124 ppmV during this long term testing period. The gas phase ammonia concentration during this time period remain fairly constant, with an average of 73 ppmV. These ammonia emissions fall just above the levels reported at the National Carbon Capture Center (NCCC) at their SSTU and PSTU during baseline MEA testing, and may be directly related to the high copper content identified in the solvent [13,14].

MEA emissions from the absorber exit appear to increase from 34 to 240 ppmV during this time period (960-1170 operating hours). These MEA emission level again are slightly lower but comparable to the reported NCCC emission levels of 100-500 ppmV [14,15].
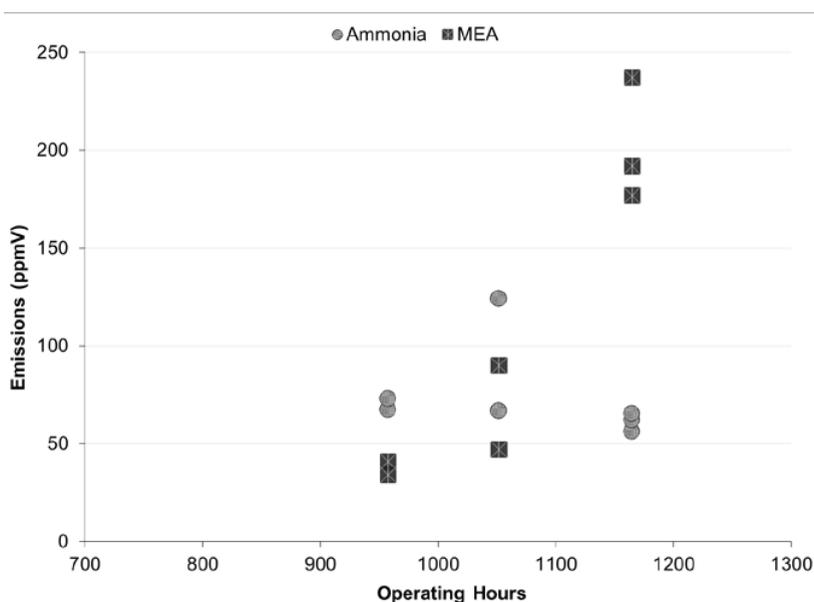

Fig. 5. Ammonia and MEA emissions from the absorber during long-term testing.

4. Conclusions

UKy-CAER successfully tested its innovative 2-stage solvent regeneration system using MEA as a baseline solvent. The overall solvent oxidation was comparable to the results from conventional amine systems test with baseline 30 wt% MEA, showing that the impact of the secondary air stripper on solvent oxidative degradation appears to be negligible.

Acknowledgements

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