Pilot plant testing to mitigate piperazine oxidation

by

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Abstract

For 5900 operating hours in 2023, The University of Texas at Austin (UT) used the Pilot Solvent Test Unit (PSTU) at the National Carbon Capture Center (NCCC) to test the Piperazine with Advanced Flash Stripper (PZAS) process under DE-FE0031861. The campaign was primarily designed to test NO₂ prescrubbing, nitrogen sparging, carbon treating, and thermal reclaiming as methods for mitigating amine oxidation. The solvent continually degraded with varying mitigation methods until a tipping point period between 4300 to 4900 hours when the ammonia emissions increased rapidly from 2.5 to 20 ppm. Thermal reclaiming by vacuum distillation after this time reduced ammonia emissions to 1.5 ppm, and removed about 90% of dissolved metals, amino acids, and heat stable salts. Ethylenediamine (EDA) and amino acids accumulated to a total of 103 mmol/kg at 4300 hours, but decreased during the tipping point period. The solvent loss for the campaign before thermal reclaiming was 0.5 kg piperazine (PZ)/tonne CO₂ captured.

 NO_2 in the flue gas was the most significant cause of oxidation. Operations were performed with and without prescrubbing by aqueous sulfite/thiosulfate to reduce NO_2 from 2.5 ppm to 0.5 ppm. Two step changes in NO_2 prescrubbing showed that it reduced the PZ oxidation rate from 0.6 mol/hr to 0.3 mol/hr. N_2 sparging in the absorber sump at 0.5 SCFM (0.03% of the flue gas rate) removed >75% of the dissolved oxygen and reduced the PZ oxidation rate by about 0.1 mol/hr. Carbon treating did not appear to have a significant effect on the amine oxidation rate.

Acid wash reduced NH_3 in the flue gas outlet from 3000 to 20 ppb, but ammonia was not removed by any water wash configuration. Total Hazardous Air Pollutants (HAPs) emissions of 50 to 270 ppb were mostly unaffected by acid or water wash. Average total amine emissions were 300–600 ppb with water wash and 0.4 ppb with acid wash.

With pumparound intercooling in the bottom section of column packing, the absorber reliably captured 95.5% of the CO₂. The maximum achieved CO₂ removal was 97.7 %. The Advanced Stripper configuration at 150 °C provided a net heat duty of 2.43 GJ/tonne CO₂.

Introduction

Amine scrubbing is one of the important technologies for CO₂ capture from combustion point sources. Deployment of this technology must address degradation of the amine by oxygen in the flue gas. Amine oxidation may produce air emissions as ammonia, listed hazardous air pollutants (HAPs) such as acetaldehyde, and unlisted hazardous pollutants such as nitrosamine. Oxidation of the amine will require disposal of spent solvent with associated environmental impacts. Oxidation also creates direct economic costs for amine makeup and solvent reclaiming.

Three mechanisms may contribute to amine oxidation.

- 1. Even if oxidation does not normally occur at absorber conditions, as with PZ, dissolved oxygen (DO) in the rich solvent will react with amine at the greater temperature in the hot rich line.
- 2. Dissolved iron ($Fe^{+2/+3}$) is a significant oxidation catalyst that is usually solubility limited. Amines degrade to amino acids and other multifunctional products that solubilize $Fe^{+2/+3}$ and increase the rate of oxidation in the absorber and rich inventory before it is heated.
- 3. NO₂ is readily absorbed from the flue gas and catalyzes oxidation by initiating free radicals in the absorber.

In NCCC 2018 test campaign, the Pilot Solvent Test Unit (PSTU) at the National Carbon Capture Center (NCCC) was modified to include the Advanced Flash Stripper to simulate the Piperazine Advanced Stripper (PZAS) process. The system was operated for 2100 hours with coal-fired flue gas containing about 1 ppm NO₂. In the last 1000 hours amine oxidation to ammonia was reduced about 13% by removing NO₂ in the SO₂ prescrubber with the addition of sodium thiosulfate and by sparging the absorber sump with 1 SCFM nitrogen. At the end of NCCC 2018, the ammonia production in the flue gas was about 5 ppm and the accumulation of total formate was 5.5 mmol/kg (Wu, 2022).

In NCCC 2019, the PZAS configuration was tested for 2000 hours with coal-fired flue gas diluted with air to 4.3% CO₂ to simulate conditions of a natural gas combined cycle (NGCC). NCCC 2019 started with the partially degraded solvent inventory from NCCC 2018. In the last 1000 hours NO₂ was prescrubbed with the addition of thiosulfate. The absorber sump was sparged with 1 SCFM of nitrogen. In the last 1000 hours the ammonia in the cleaned flue gas was about 4 ppm. In the last 450 hours of NCCC 2019, carbon treating of the rich solvent reduced ammonia (NH₃) T 4.5 to 3 ppm and decolorized the solvent. The final total formate was 40 mmol/kg (Wu, 2022).

In 2022 the pilot plant at the Separations Research Program (SRP 2022) at UT was operated for 700 hours with PZAS using air/CO₂ blended to NGCC conditions. At 250 hours the synthetic flue gas was spiked for 215 hours with 1 ppm NO₂ resulting in oxopiperazine production of 7.8 mol/mol NO₂. Total formate at the end of SRP 2022 was 5.3 mmol/kg (Chen, 2024).

The primary objective of this pilot plant campaign (NCCC 2023) with PZAS in the PSTU was to test in sustained operation the mitigation of amine oxidation by NO_2 prescrubbing, N_2 sparging, carbon treating, and thermal reclaiming.

Pilot plant logistics

A pilot plant campaign was performed in the PSTU with the PZAS process (30 wt % PZ) using the advanced flash stripper with gas boiler flue gas diluted with air to 4.3% CO₂ (Figure 1). The objective was to test methods to mitigate amine oxidation with and without NO₂ in the flue gas.

The campaign used the PSTU from December 2022 to October 2023. The campaign started on December 8, 2022, and stopped on December 22, 2022, followed by a two-month break until February 22, 2023, after which operation continued mostly uninterrupted until October 20, 2023. The campaign tested for 5900 operating hours the performance of PZAS to capture about 6 tonnes CO_2/day , as shown in Table 1.

Flue gas conditions	Gas fired boiler diluted with air and heated		
Т	°C	110	
Р	Atm	1.085	
Flow	kg/hr	3629	
CO ₂	dry mol %	4.3	
O ₂		13.2	
H ₂ O	moi %	8	
Solvent Inventory	gal	1500	
Absorber packing	ft	2 x 20	
Stripper sump T	°C	150	
Stripper P	bara	5.3	

Table 1: Parameters of the NCCC 2023 campaign

The solvent used was 5 m PZ (30 wt %) at a lean loading of 0.2 mol CO₂/equiv N. Partially degraded solvent from NCCC 2019 and SPR 2022 was combined with about the same amount of clean PZ. The initial total formate was about 5 mmol/kg. The absorber was operated with in-and-out intercooling (IO IC) from December 8, 2022 until the first shutdown on December 22, 2022. After March 7, 2023 an absorber with pump-around intercooling (PA IC) was used.

The campaign focused on testing long-term operation using NGCC flue gas. In NCCC 2019 (Gao & Rochelle, 2020), the flue gas was fed to the absorber at approximately 76.6 °C with 4.3% CO₂. Before NCCC 2023, a flue gas heater was installed at NCCC allowing for the flue gas to be delivered at 110 °C. These conditions represent the flue gas in the Mustang FEED (Rochelle et al., 2024). The campaign also included parametric testing to measure absorber performance at atypical operating conditions. These included operation without a lean solvent trim cooler, which brought the temperature up to 65.5 °C, and operation at a lean loading of 0.18 mol CO₂/equiv N, for which three different solvent rates were tested.

On the stripper side of the process, both heat duty and heat loss of the stripper system were measured. Heat loss was measured using energy balances and was combined with previous data for the same system to qualitatively explain the impact of process and ambient conditions on heat loss. During the 2023 campaign, the heat duty of the stripper was measured using steady-state pilot plant data over 60-minute intervals. One of the objectives was to measure heat duty at high CO₂ removal (93–97%), which was found to benefit economics of the capture plant (Suresh Babu et al., 2023). Heat duty was also measured in the presence of a hot flue gas with high water content, hot lean solvent, low lean loading (0.18–0.2 mol/equiv N), and high total bypass split fraction. Heat duty was measured and optimized for absorber configurations using PA IC configurations.



Figure 1: The PZAS flowsheet for the NCCC 2023 campaign

Four methods were tested to mitigate amine oxidation:

- 1. The diluted flue gas containing about 2.5 ppm NO₂ was prescrubbed with aqueous NaSO₃/Na₂S₂O₃ to reduce the NO₂ to about 0.5 ppm.
- 2. Dissolved oxygen in the rich solvent was removed by sparging with 2.0 SCFM nitrogen in the sump of the absorber.
- 3. Rich solvent was cleaned by carbon treating to remove chelated, dissolved iron ($Fe^{+2/+3}$).
- 4. Reclaiming by batch distillation was performed near the end of the campaign to remove large degradation products that solubilize $Fe^{+2/+3}$.

Table 2 shows the timeline for the mitigation methods with the black color indicating that the mitigation method was on.

Weeks	1–7	7–12	12–17	17–22	22–30	30–35
Hours	0– 1249	1249– 2035	2035– 2869	2869– 3711	3711– 5156	5225-5923
Carbon treating						
Reclaiming						
NO ₂ prescrubbing						
N ₂ sparging						

Table 2: 2023 NCCC pilot campaign timeline

Indicators of Solvent Oxidation

Ammonia

Ammonia is an indicator of PZ oxidation. It is produced in the initial stages of PZ oxidation and further produced by the oxidation of the degradation products of PZ. Figure 2 shows ammonia measured by FTIR in the clean gas from the water wash. With a starting solvent that was already partially degraded, ammonia production started at 2 ppm. With all mitigation methods on and nitrogen sparging off, ammonia decreased to 1 ppm. When NO₂ scrubbing was also off and in the following period when all the mitigation methods were off, ammonia increased to 9 ppm. When all the mitigation methods were restored, the ammonia production decreased to 3 ppm. At 4400 hours there was a "tipping point" after which the ammonia production rapidly increased to 20 ppm. After thermal reclaiming removed the less volatile degradation products and dissolved metals, ammonia decreased to 1.5 ppm, because the oxidation rate of the PZ was reduced and because there was a lower concentration of amino acids and other non-volatile degradation products that could be oxidized to produce ammonia.



Figure 2: NH₃ measured by FTIR at water wash inlet/outlet and absorber outlet in NCCC 2023

Dissolved metals

Figure 3 shows the accumulation of dissolved Fe, Cr, Mn, and Ni measured by ICP-MS. Ni and Mn increased consistently throughout the campaign suggesting that they are reliable indicators of stainless steel corrosion.

An episode of stainless steel corrosion at 2030–2370 hours was apparently initiated by turning off the NO_2 prescrubbing. It showed increases in all four metal ions consistent with corrosion of a stainless steel containing Mn.

A more intense episode at 4300–5000 hours showed no increase in Mn consistent with corrosion of a stainless steel without Mn at a different location. The second episode also corresponds to the "tipping point" with the rapidly increasing production of ammonia.

Stainless steel corrosion is known to occur at high temperature at reducing conditions (Liu, 2022). The changing oxidation conditions of the process may have resulted in strongly reducing conditions at specific locations at the high temperature around the stripper and its heat exchangers. All the dissolved metals were effectively removed by the thermal reclaiming.

316L and 304 stainless coupons located throughout the process showed no significant corrosion based on the thickness of the coupon, so the two corrosion events were likely not distributed throughout the plant and must have occurred at specific, unknown, exposed points in the equipment. In NCCC campaigns in 2018 and 2019, 316L coupons at hot rich and hot lean sample points showed corrosion rates of 400 to 1400 mm/yr. these corrosion rates were estimated by weighing the coupons after the removal corrosions products from the surface.

Dissolved iron fluctuated during the campaign. Previous work has suggested that its concentration is frequently limited by the solubility of the Fe^{+2} or Fe^{+3} species (Wu, 2022). Its concentration would decrease with a general shift to more reducing conditions since the Fe^{+2} species is less soluble in loaded PZ. Dissolved iron would increase as it is chelated by an increasing concentration of amino acids. $Fe^{+2/+3}$ is an oxidation catalyst so its variation and its general increase would also affect the rate of amine oxidation and ammonia production.

Dissolved Cr generally increases but there are periods where it appears to be removed by carbon treating. It is listed as a hazardous dissolved metal and can result in classification of liquid or solid waste as "Hazardous", requiring more expensive disposal methods. Its maximum concentration in solution (290 ppm) is well above 5 ppm, the leachate limit that would class solid waste as "Hazardous".



Figure 3: Dissolved metal ions in solvent by ICP-MS in solvent for NCCC 2023

Amino acids/Nitrogen balance

A new analytical method was brought online after NCCC 2023 to determine the concentration of amino acids. A high resolution (50,000) quadrupole time-of-flight mass spectrometer (QTOF-MS) coupled to a high-performance liquid chromatograph (HPLC) was used to screen degraded PZ samples and identify amino acids by accurate m/z determination. Five amino acids with significant concentrations were quantified with calibration standards by HPAE-PAD (high performance anion-exchange chromatography with pulsed amperometric detection). Samples were hydrolyzed for 24 hours with an equal volume of 50% NaOH to convert amides and lactams to the free amino acid anions.

Figure 4 shows the development of the concentrations of the five amino acids. The total concentration of amino acid anions (as N/2, equivalent to PZ) started at 25 mmol/kg and increased to 103 mmol/kg before it was reduced to 12 mmol/kg by thermal reclaiming. At 4600 hours the total amino acid (103 mmol/kg) was significant compared to the sum of other liquid degradation products (134 mmol/kg, EDA+AEP+NFPZ+OPZ+MPZ+total formate). It was also greater than the cumulative ammonia/2 produced up to that point (0.



204 mmol/L).

Figure 4: Hydrolyzed Amino acid degradation products in lean solvent

Heat Stable Salts

Figure 5 shows the moles of the total formate in the solvent. Rich samples were hydrolyzed for 24 hours with an equal volume of 10 N NaOH to convert amides to free acids. These samples were then analyzed by anion chromatography.

The production of formate started slowly as it is probably not produced by the first step of PZ oxidation. Rather the formate is produced by the oxidation of degradation products such as EDA

and amino acids that must accumulate. The production rate of formate accelerated rapidly after the tipping point was reached. Figure 5 show that total formate production nicely tracks total NH_3 production with a ratio of 4.5 mol NH_3 /mol total formate.

Reclaiming removed most of the heat stable salts and amino acids (Figure 5), so after reclaiming the concentration of total formate was much lower and its rate of production was reduced to that at the beginning of NCCC 2023.



Figure 5: Cumulative emissions of ammonia and moles of total formate in rich samples hydrolyzed for 24 hours with an equal volume of 10 N NaOH.

Mitigation Methods

NO2 Prescrubbing

 NO_2 prescrubbing was used to test the effect of NO_2 in the inlet flue gas on the oxidation of PZ. Suresh Babu (2019) showed that the addition of thiosulfate to the SO₂ prescrubber is effective in removing NO_2 from coal-fired flue gas containing 50 ppm. Since SO₂ is not available in gas-fired flue gas, sodium sulfite must also be added to the prescrubber. In the PZAS FEED design for NGCC (Rochelle et al., 2022) there is also no prescrubber. Because of the annual cost of sodium sulfite makeup and the capital cost of the additional prescrubber, it is unlikely that this technology is a practical mitigation method. However, its use in this campaign was intended to demonstrate the value of other technologies to reduce NO_2 , such as selective catalytic reduction (SCR) with ammonia.

 NO_2 was effectively removed from the inlet flue gas by scrubbing with an aqueous solution of sodium sulfite (Na_2SO_3) and sodium thiosulfate ($Na_2S_2O_3$). After dilution with air to 4.3% CO₂ (dry) the raw flue gas contained about 2.5 ppm NO₂. For most of the campaign the addition rate

of Na₂SO₃ was 180 gmol/week; this was increased to 540 gmol/week for the last 5 weeks, equivalent to $9.5-19 \text{ mol NaSO}_3/\text{mol NO}_2$ in the flue gas. After an initial charge, the addition rate of Na₂S₂O₃.5H₂O was 50 gmol/week; it was increased to 200 gmol/week at 3700 hours, equivalent to $0.9-3.5 \text{ mol Na}_2$ S₂O₃/mol NO₂.

Mononitrosopiperazine (MNPZ) is produced by the overall reaction of NO₂ with PZ, but thermal decomposition of MNPZ at 150 °C in the stripper sump provided an acceptable steady-state concentration. Figure 6 shows mononitrosopiperazine in the lean solvent. It is expected that one mole of nitrosamine will be formed for every mole of absorbed NO₂. However for the period starting at 2000 hrs, the estimated stoichiometry was only 0,41 mol nitrosamine formed/mole NO₂ absorbed. So 59% of the nitrite formed from NO₂ must be reacting with degradation products rather than with piperazine. The steady-state concentration should depend on the state of the NO₂ prescrubber and the level in the stripper sump. The time to reach steady state appears to be several weeks. With NO₂ prescrubbing and 30% stripper sump level in the first 2000 hours, MNPZ was approaching 1.2 mmol/kg. When NO₂ scrubbing was turned off from 2000 to 3200 hours, MNPZ increased to 3.1 mmol/kg. When the stripper sump level was increased from 30 to 70%, increased thermal decomposition reduced the MNPZ to 2.3 mmol/kg. With NO₂ scrubbing back on from 3200 to 4900 hours, MNPZ steadily decreased to 0.3 ppm.



Figure 6: Mononitrosopiperazine in rich solvent determined by HPLC

Figure 7 shows the accumulation of degradation products and cumulative loss of nitrogen represented as N_2 . The rate of N_2 loss is estimated as the slope in each operating period. A change in slope can be attributed to change in the NO₂ scrubbing. The most significant changes occurred at 2000 hours when the NO₂ prescrubber was turned off (nitrogen loss (as N/2)) increases from 0.3 to 0.6 moles/hr) and when all the mitigation methods including NO₂ scrubbing were turned back on at 3700 hours (nitrogen loss as N/2 decreases from 0.6 to 0.2 moles/hr). If these step changes are attributed solely to NO₂ absorption, they correspond to an apparent stoichiometry of 1.8 and 2.4 moles PZ oxidized/mole NO₂ absorbed, respectively.

More details on NO_2 scrubbing and the effects of NO_2 on PZ oxidation are given in the dissertation by Chen (2024).



Figure 7: Total moles of N/2 in degradation products in the lean solvent, including cumulative ammonia. The red values represent the regressed slope at that section of the data.

Nitrogen sparging/Dissolved Oxygen

DO carried over in the rich solvent may play a role in amine oxidation in the rich storage tank and downstream heat exchangers. For most of the campaign nitrogen was sparged at 2 SCFM into the absorber sump to strip out the DO. At 4400 hours the rate was reduced to 0.5 SCFM. The single sparge pipe in the absorber sump was a 12-inch long sintered porous tube constructed of Mott 316 stainless steel Media Grade 2 material (Mott 2308-A04-12-A00-GAS-AB) with a sparge cross-sectional area of 0.13 ft². More details are available in Closmann et al. (2024).

Online DO measurements were made at the absorber intercooler (IC) loop and the rich amine downstream of the rich amine tank in real time throughout the campaign (Figure 8); the IC loop location is generally representative of the DO concentration in the absorber sump. In early April 2023 ~1,250 hours into the campaign, the N₂ gas sparging in the absorber sump was shut off for an extended period. The DO measurement downstream of the rich amine tank settled at approximately 1.8 mg/L whereas it was ~4 mg/L in the IC loop during this same time. These data indicate that approximately half of the residual DO in the rich amine reached the downstream probe location. It is therefore highly probable that little if any DO is left in the rich solvent that enters the stripper and little oxygen will be present in the produced CO₂. Online measurement of oxygen in the product CO₂ was consistently less than 1 ppm, confirming that practically all the DO is consumed by amine oxidation before the stripper.

The full set of DO data from March 2023 through the end of the campaign is plotted in Figure 9. Those data demonstrate that as the campaign progressed and the PZ solvent became oxidized, the residual DO downstream of the rich amine tank decreased to <0.1 mg/L exhibiting >98% DO consumption (September 5, 2023) compared to DO measurements in the IC loop from early in the

campaign. Immediately upon reclaiming the solvent two weeks later, the residual DO at the downstream location increased to the range of 0.8 mg/L, indicating that the oxidation processes in the solvent had been reduced through removal of readily oxidizable degradation intermediates including aldehydes, which are themselves readily oxidized. The data in Figure 8 also demonstrate that online DO measurement in the rich amine will be a useful tool for monitoring the general level of oxidation occurring in the solvent in a commercial application.



Figure 8: DO probe locations during the NCCC campaign



Figure 9: Online DO measurements during NCCC 2023

Figure 10 is a plot of DO measurements collected at the IC loop location while performing short-term N_2 sparge rate step changes. The short-term tests started with a sparge rate of 2 SCFM N_2 gas, resulting in a DO concentration of ~0.45 mg/L. When the N_2 sparge rate was increased to 4

SCFM, the DO concentration increased to >0.6 mg/L. When the N₂ sparge rate was decreased to 1 SCFM, the DO concentration in the IC loop decreased to ~0.35 mg/L. Finally, the N₂ sparge rate was reduced to 0.5 SCFM at 4500 hours and the resulting DO concentration was reduced to ~0.25 mg/L. Note that a consistent diurnal variation in the DO data occurred and was generally believed to be a result of daily temperature changes from daytime to nighttime. These results indicate that the optimal N₂ sparge rate was the lowest rate tested (0.5 SCFM). With a flue gas rate of 2,000 SCFM, the N₂ gas rate of 0.5 SCFM was <0.03% of the total gas traffic through the absorber column.



Figure 10: DO probe measurements over a range of N₂ sparge rates

Carbon Treating

Carbon treating was implemented with an existing system on the PSTU at NCCC (Figure 11). The treating vessel has 14 poles with 2 canisters per pole. Each tin-plated carbon steel canister is 11 inches OD x 22 inches long with 31 lbs of granular activated carbon derived from coconut shells. 11 poles were blanked off and only 6 canisters on 3 poles were active. 15 gpm of rich solvent (about the same flow as the rich solvent to the stripper) was pumped from the rich storage tank to the carbon vessel and returned by gravity flow to the rich storage tank. At this condition the liquid level in the carbon vessel was at the top of the canisters.

Figure 12 demonstrates the effect of carbon treating on the UV absorbance of the solvent. Wu (2022) showed in bench-scale experiments the activated carbon used by NCCC would remove the degradation compounds causing the UV absorbance. Wu also demonstrated that this compound was a form of chelated Fe^{+3} . At 1100 hours and 3680 hours the used carbon canisters were replaced with fresh carbon. The fresh carbon immediately removed 40 to 50% of the compounds causing the UV absorbance.

It appears that fresh carbon also catalyzed the consumption of DO. Approximately 2900 hours into the campaign, the carbon bed was taken offline and the associated solvent was transferred to the rich amine tank. The aggregate residence time of the rich amine solvent held in the absorber sump, absorber packing (holdup), rich amine tank, and carbon vessel was comparable to the rich amine residence time immediately after rich solvent was transferred from the carbon vessel to the rich amine tank. Immediately following the rich amine transfer, the DO in the rich amine increased to $\sim 2.5 \text{ mg/L}$. This observation indicates that the carbon bed may have behaved as a catalyst for oxidation of PZ and/or degradation intermediates.

Further analysis of the carbon treating performance at NCCC 2023 will be given in Plantz and Rochelle (2024).



Figure 11: Carbon vessel with canisters mounted on poles



Figure 12: UV absorbance at 230 nm reduced by carbon treating and reclaiming

Reclaiming

About 1 gpm of lean solvent was fed to a semicontinuous, batch distillation column at 150 °C/vacuum for 65 hrs, treating three inventories of solvent. Condensed aqueous PZ was returned to the solvent loop. The bottoms of the column was collected as a waste for disposal. Additional details are available in Stevens et al. (2024).

The thermal reclaiming removed practically all the nonvolatile degradation products and impurities and a large fraction of other components less volatile than PZ:

>99% UV absorbance, Cr, oxoPZ
>94% Fe, PZAA, OPZA
>87% NFPZ, HZZ, AEP
>86% total amino acids + ethylenediamine

Reclaiming the solvent reduced the visible color from a brownish orange to light yellow (Figure 13). It also reduced the UV absorbance at 320 nm by a factor of 80 (Figure 12). Dissolved metal ions (Figure 3) were reduced by 94% (Fe) to 99% (Cr).

After reclaiming, the rate of production of total nitrogen degradation products decreased to the value measured at the beginning of the campaign.



Figure 13: Color of rich solvent from beginning to end of thermal reclaiming

Figure 14 shows the total inventory of PZ estimated from solution analysis and tank levels. About 600 kg PZ was lost before reclaiming (0.51 kg PZ/tonne CO_2 removed). Depending on the estimating method, 290 to 480 kg PZ was removed by the reclaiming operation. NaOH was not added to the reclaimer. It is expected that the judicious use of NaOH to neutralize heat stable salts and decompose amides of PZ would significantly reduce PZ loss during reclaiming.



Figure 14: PZ inventory

Emissions

The composition of the cleaned gas leaving the water wash was measured in the last 2200 hours by PTR-ToF-MS. The single-stage water wash was used for most of the campaign. Four additional water wash configurations were tested in this period. A two-stage water wash and a water wash followed by an acid wash were also tested. Figure 15 shows the acid wash configuration.



Figure 15: Absorber flowsheet with wash tower operated as acid wash

Emissions averages are presented in Figure 16 for four periods..Three periods represent singlestage water wash at "normal" conditions, maximum degradation, and post-reclaiming. The fourth period represents acid washing. Compounds were grouped as ammonia, combined amines, other nitrogen-containing species including slightly acidic nitrosamines, pyrazines, acetamide and pyrroles, and combined HAPs. For all periods except acid washing the dominant emissions were ammonia, followed by combined amine species, which includes PZ, MPZ, EPZ, EDA, N-methylethylenediamine (MEDA), 1-formylpiperazine (NFPZ), 1-(2-aminoethyl)piperazine (AEP), methylamine, ethylamine, and other PZ derivatives.

The single-stage water wash reduced the combined amine emissions to 300–600 ppb. With acid wash the combined amine emissions were 0.4 ppb. Other two-stage water wash configurations also reduced combined amines to 0.4 ppb.

The acid wash configuration reduced average ammonia emission to 20 ppb. Other wash configurations removed little ammonia. The variation of the ammonia emissions from 900 to 15,000 ppb represents changes in other process conditions.

The average combined HAPs varied from 70 to 200 ppb and were generally not removed by the water wash or acid wash. The lowest value (50 ppb) occurred after thermal reclaiming when the general rate of amine oxidation was also reduced.



Figure 16: Combined average emissions for each of four operating periods

"Tipping Point"

There was a tipping point in system performance at 4300 hours that lasted for at least 700 hours. The endpoint of the period was confounded by taking carbon treating off at 4982 hours and by the initiation of thermal reclaiming at 5156 hours. The other three mitigation methods were used in this period.

This was a major corrosion event as dissolved iron increased from 0.02 to 1.4 mmol/kg and dissolved Cr increased from 0.1 to 5.5 mmol/kg. NH₃ emissions increased from 2.5 to 20 ppm. Total heat stable salts increased from 40 to 100 mmol/kg, consistent with an increase in ammonia production from 1600 to 3100 gmols. The UV absorption increased at a significantly faster rate after the tipping point, consistent with a greater concentration of Fe⁺³ (Figure 3). The apparent production rate of total nitrogen degradation products did not change (Figure 7) and was about the same as the beginning of the campaign with all the mitigation methods. Emissions of the HAPs increased from 50 to 250 ppb with an average value of 200 ppb in the tipping point period (Figure 16), somewhat tracking ammonia emissions and production of heat stable salts.

There is no clear explanation of the tipping point. The corrosion episode was probably caused by highly reducing conditions at the high temperature of the stripper, known to result in stainless steel corrosion. Carbon treating appeared to minimize stainless steel corrosion in NCCC 2019 (Liu, 2022). Carbon treating may have prevented stainless steel corrosion during most of the NCCC 2023 campaign, but may also have been ineffective at the tipping point because the carbon was saturated.

Energy and Capture performance

The absorber with pump-around intercooling (PA IC) maintained an average of 95.5% CO2

removal for approximately 4000 hours of operation. The lean loading was 0.2 mol/equiv N with an average rich loading of 0.4 mol/equiv N. The heat duty was minimized using an evolutionary optimization procedure with sequential step changes in the cold rich and warm rich solvent bypasses. The minimum net heat duty was 2.43 GJ/tonne with bypasses of 5% cold rich and 64% warm rich (Figure 17). Successful parametric testing during the campaign included a low lean loading of 0.18 mol/equiv N and operation without a lean solvent cooler.



Figure 17: Comparison between measured and modeled heat duty during long-term testing. This period included operation with the absorber in IO IC and PA IC configurations; rich loading = 0.37–0.41 mol/equiv N; lean loading = 0.2 mol/equiv N; stripper sump temperature = 150 °C

The performance of the absorber and stripper was accurately estimated by the rate-based models with an average error below 5%. The validated absorber model was used to study absorber design. With a rich loading of 0.4 mol CO_2 /equiv N and no lean solvent cooler, the calculated CO_2 removal decreased from 97 to 90% when the PA IC temperature increased from 26.6 to 40 °C (Figure 18). The feasibility of a design without a lean solvent cooler is contingent on the ability to maintain the PA IC temperature throughout the year (Abreu, 2024; Abreu et al. 2024).



Figure 18: Simulated performance of an absorber with PA IC and without a lean solvent cooler. Lean solvent varied from 3,000 to 9,000 kg/hr. With PA IC at 80 °F, the system can achieve a CO₂ removal of 97% while maintaining an acceptable energy performance.

The model demonstrated that the NCCC absorber could not achieve greater than 98.6% CO₂ removal without water condensing in the absorber (Figure 19). This water condensation limit will be present for all aqueous capture solvents with equilibrium constraints. Operating above this limit will require process modifications to enable water balance control and volatiles removal in the water wash or the addition of a direct contact cooler upstream of the absorber to avoid water condensation.



Figure 19: Maximum CO₂ removal before the onset of water condensation in the absorber. Achieving a greater CO₂ removal will require a DCC upstream of the absorber to maintain operation with water evaporation in the absorber. All runs shown are water balanced.

Conclusions

- Single-stage thermal reclaiming of three solvent inventories reduced the apparent oxidation rate to the value at the beginning of NCCC 2023. It reversed the NH₃ and DO trends of the tipping point period and removed >95% of the dissolved metal ions and 86% of the amino acids.
- NO₂ prescrubbing reduced the PZ oxidation rate from 0.6 mol/hr to 0.3 mol/hr with makeup rates of 9.5–19.0 mol NaSO₃/mol NO₂ and 0.9–3.5 mol Na₂S₂O₃/mol NO₂.
- N_2 sparging at 0.5 SCFM (0.03% of the flue gas) in the absorber sump removed >75% of the dissolved oxygen and reduced the PZ oxidation rate by about 0.1 mol/hr.
- The effects of carbon treating on amine oxidation were not conclusive. It reduced UV absorption, decomposed nitrosamine, and appeared to catalyze oxygen consumption.
- Total amino acids were a major product that accumulated to 103 mmols/kg at 4200 hours.
- The solvent reached an unexplained "tipping point" approximately 4300 hours into the campaign with significant accumulation of stainless steel metal ions and a rapidly increasing ammonia concentration.
- NH₃ was not removed by water wash, but acid wash reduced NH₃ in the flue gas outlet from 7 ppm to 20 ppb.
- Total HAPs were mostly unaffected by water wash and acid wash and varied from 70 to 200 ppb.
- The solvent loss for the campaign before thermal reclaiming by overall material balance was 0.5 kg PZ/tonne CO₂ captured.
- With pump-around intercooling in the bottom, the absorber reliably captured 95.5% of the CO₂. The maximum achieved CO₂ removal was 97.7 %.
- The Advanced Stripper configuration at 150 °C provided a net heat duty of 2.43 GJ/tonne CO₂.

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