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LAUNCH D5.2.4 Piperazine Oxidation by NO<sub>2</sub>

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# 1 Introduction

This LAUNCH deliverable has results of investigating Piperazine Oxidation by  $NO_2$ , performed by the University of Texas.

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# Piperazine Oxidation by NO<sub>2</sub>

Quarterly Report for January 1 – March 31, 2023

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## Abstract

Amine oxidation is a significant concern in deploying amine scrubbing for  $CO_2$  capture from postcombustion flue gas. Oxidation is believed to be caused by dissolved oxygen at elevated temperatures,  $Fe^{3+}/Fe^{2+}$  shuttling between the absorber and the stripper, and catalysis by NO<sub>2</sub> in the absorber. Amine selection, dissolved oxygen removal, and solvent reclaiming mitigate oxidation due to dissolved oxygen and  $Fe^{3+}/Fe^{2+}$ , but not by NO<sub>2</sub>. NO<sub>2</sub> at 0.5–5 ppm appears in pilot plant testing to cause significant amine oxidation. The absorption products of NO<sub>2</sub> include nitrite and amine radicals. Nitrite reacts with amines to form carcinogenic nitrosamines, and amine radicals initiate radical propagation, oxidizing more amines. To ease the serious oxidation and environmental impacts caused by NO<sub>2</sub>, only power plants with selective catalytic reduction (SCR) should be retrofitted for carbon capture and applying an NO<sub>2</sub> prescrubber before the absorber further decreases the concentration of NO<sub>2</sub> in the flue gas.

The 2023 NCCC pilot plant campaign uses flue gas from the gas-fired boiler containing 2.5 ppm  $NO_2$  and no  $SO_2$ . The  $NO_2$  prescrubber is operated with a target < 0.5 ppm  $NO_2$  concentration entering the absorber to investigate the oxidation by  $NO_2$  and test the scrubbing effect of sulfite/thiosulfate. This report summarizes the preliminary data of the  $NO_2$  prescrubber and the generation of mononitrosopiperazine (MNPZ) in the amine scrubbing system.

# Introduction

Post-combustion coal flue gas typically has 0.5-5 ppm NO<sub>2</sub> and 10-100 ppm NO. NO<sub>2</sub> is easily absorbed by reacting with amines to form amine radicals and nitrite (NO<sub>2</sub><sup>-</sup>) in the absorber. 5m piperazine (PZ) absorbs about 50% of the inlet NO<sub>2</sub> and produces nitrosamines, according to the 2022 SRP pilot plant campaign (2022, Chen). The solubility of nitric oxide (NO) is low, resulting in negligible nitrosation. However, NO may be oxidized to NO<sub>2</sub> in the presence of oxygen in the ductwork and the absorber (Moser, 2022).

The abundant absorption product, nitrite, attacks piperazine carbamate and produces mononitrosopiperazine (MNPZ), especially at the high temperature in the stripper. Because PZ is thermally stable, the stripper can be operated up to 150 °C, and this high temperature will accelerate the degradation of MNPZ and thus limit its accumulation (Fine, 2015). The pilot plant

results from campaigns at UT SRP, CSIRO Tarong, and Pilot Plant 2 (PP2) demonstrated that MNPZ was significantly degraded in the high-temperature stripper and generally stayed below 5 mM (Nielson, 2018).

NO<sub>2</sub> absorption produces amine radicals that may propagate the free radical oxidation of amines. Hypotheses are presented in Figures 1 and 2. Amine radicals will propagate by reacting with dissolved oxygen and PZ before the termination step. In this case, the number of moles of amine oxidized by one mole of NO<sub>2</sub> remains unknown. In addition to oxidizing PZ, the radicals can further oxidize degradation products such as piperazin-2-ol (PZOH) into 2-oxopiperazine (OPZ). NO<sub>2</sub> and its radical products can also be involved in an iron redox reaction, a one-electron transfer process.

As a result, prescrubbing NO<sub>2</sub> from the flue gas is crucial for reducing solvent oxidation and controlling MNPZ generation. NO<sub>2</sub> prescrubbing by sulfite and thiosulfate has been applied successfully in two piperazine (PZ) pilot plant campaigns at the National Carbon Capture Center (NCCC) in 2016 (Selinger, 2018), and 2018–19 (Suresh Babu, 2019). The reactions are summarized in Figure 3. SO<sub>2</sub> in the flue gas reacts with hydroxides to form sulfite. Sulfite removes NO<sub>2</sub> and generates nitrite and sulfite radicals. The radical propagation by dissolved oxygen makes sulfite consumption fast. Therefore, the addition of thiosulfate slows down the sulfite consumption rate by competing with sulfite to react with SO<sub>5</sub><sup>-</sup> •.

In the 2016 and 2018–19 campaigns, 90% NO<sub>2</sub> removal required 25 mM sulfite, which was maintained with 50 mM thiosulfate. In addition to the concentrations of sulfite and thiosulfate, these two campaigns concluded that the NO<sub>2</sub> removal efficiency also depended on the pH and the prescrubber sump level. A more alkaline environment (pH > 8) seemed to suppress the sulfite oxidation and increase the NO<sub>2</sub> removal efficiency because of the lower HSO<sub>3</sub><sup>-/</sup>SO<sub>3</sub><sup>2-</sup> ratio; SO<sub>3</sub><sup>2-</sup> absorbs NO<sub>2</sub> faster than HSO<sub>3</sub><sup>-</sup>. The pH of the prescrubber changes with the absorption of NO<sub>2</sub> and CO<sub>2</sub>, and the formation of N-S compounds, especially hydroxylamine disulfonate, which is the initial product N-S degradation reactions (Figure 3). The lower tank liquid level (< 50%) might decrease the thiosulfate oxidation due to shorter residence time.

The most significant difference in the current 2023 NCCC campaign is that there is no  $SO_2$  in the flue gas while there was 20-40 ppm SO<sub>2</sub> in the previous two campaigns. SO<sub>2</sub> is the only source of sulfite; as a result, sulfite is added to the prescrubber intermittently to test the its efficiency and to keep the  $NO_2$  concentration entering the absorber under 0.5 ppm. When the  $NO_2$  prescrubber is on, 150 lb of sodium sulfite is added weekly, sodium thiosulfate is added as needed, pH is controlled at 8.5–9.0 by NaOH, and sodium sulfate concentration is held below 2 M by bleeding or water addition to avoid sodium compound precipitation. Tank level control is sacrificed as a tradeoff for the pH control and the sodium concentration control. There are three on-line NO<sub>2</sub> analyzers monitoring the boiler, absorber inlet, and absorber outlet concentrations. Prescrubber liquid samples are treated with 37% formaldehyde aqueous solution at 5:1 v/v ratio to stop sulfite oxidation during transportation from NCCC to Austin. The current campaign started in mid-December 2022, shut down due to freezing temperatures around the last week of December and again for plant maintenance from mid-January to mid-February, and started again on February 22, 2023. To understand the influence of NO<sub>2</sub> removal on amine oxidation, this campaign starts with the NO<sub>2</sub> prescrubber on for 10 weeks, followed by 10 weeks of operation without removing NO<sub>2</sub>, and then turning the NO<sub>2</sub> prescrubber back on for the final 6 weeks of the campaign.

Absorber NO<sub>2</sub> absorption: Iron oxidation:  $PZ + NO_2 \rightarrow PZ \cdot + NO_2^ Fe^{2+} \xrightarrow{DO, NO_2, \cdot OH, R} Fe^{3+}$ Radical propagation:  $PZ \cdot + O_2 \rightarrow PZOO \cdot$ Organoperoxy dissociation:  $R \cdot + PZ \rightarrow PZ \cdot + P$  $PZOOH + PZ \rightarrow 2PZOH$  $R \cdot = PZOO \cdot, PZO \cdot, and \cdot OH$  $PZOOH \rightarrow PZO + \cdot OH$ P = PZOOH, PZOH, and  $H_2O$  $Fe^{2+} + PZOOH \rightarrow Fe^{3+} + PZO^{-} + \cdot OH$ **Radical termination:**  $Fe^{3+} + PZOOH \rightarrow Fe^{2+} + PZOO \cdot + H^+$  $2PZ \cdot + H_2O \rightarrow PZOH + PZ$ 

PZOH or similar products might go through the same reactions



▶ NO<sub>2</sub> + n PZ → degradation products (PZOH → OPZ → EDA → NH<sub>3</sub>, formate...)

Figure 1: PZ oxidation by NO<sub>2</sub> and the synergy of NO<sub>2</sub> and iron



Figure 2: PZOH oxidation by NO<sub>2</sub> hypothesis

# Major reactions:

Sulfite generation:  $SO_2 + NaOH \rightarrow SO_3^{2-}$ NO<sub>2</sub> absorption:  $NO_2 + SO_3^{2-} \rightarrow NO_2^{-} + SO_3^{-} \cdot$  $2NO_2 + HSO_3^{-} + H_2O \rightarrow 2NO_2^{-} + SO_4^{2-} + 3H^+$  (slower)

Sulfite oxidation (radical chain reactions): 
$$SO_3^{-} + O_2 \rightarrow SO_5^{-} \cdot$$
  
 $SO_5^{-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^{-} \cdot$   
 $SO_4^{-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^{-} \cdot$   
 $2SO_3^{-} \cdot \rightarrow S_2O_6^{2-}$   
Thiosulfate radical scavenger:  $SO_5^{-} \cdot + S_2O_3^{2-} \rightarrow SO_5^{2-} + S_2O_3^{-} \cdot$   
 $SO_5^{2-} + SO_3^{2-} \rightarrow SO_5^{2-} + S_2O_3^{-} \cdot$   
 $SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-}$   
 $2S_2O_3^{-} \cdot \rightarrow S_4O_6^{2-}$   
 $S_4O_6^{2-} + SO_3^{2-} \leftrightarrow S_3O_6^{2-} + S_2O_3^{2-}$ 

#### Side reactions:

CO<sub>2</sub> absorption : 
$$CO_2 + 0H^- \rightarrow CO_3^{2-} + H^+$$
  
 $CO_3^{2-} + CO_2 + H_2O + 2H^+ \rightarrow 2HCO_3^-$   
 $2HCO_3^- + SO_2 + 0.5 O_2 \rightarrow SO_4^{2-} + 2CO_2 + H_2O$ 

Nitrite reactions: 
$$NO_2^- + 2HSO_3^- + H^+ \rightarrow HON(SO_3)_2^{2-} + H_2O$$
 (Hydroxylamine disulfonate)  
 $HON(SO_3)_2^{2-} \rightarrow HN(SO_3)_2^{2-} + HOHN(SO_3)^- + HONH_2 + H_2N(SO_3)^- ...$ 

#### Figure 3: NO<sub>2</sub> removal by sulfite and thiosulfate

### Analytical Methods

#### Hot gas FTIR

Hot gas Fourier-transform infrared spectroscopy (FTIR) is used to measure infrared active compounds, including NO<sub>2</sub> (> 5 ppm), CO<sub>2</sub>, PZ, H<sub>2</sub>O, NH<sub>3</sub>, and acetaldehyde, by molecular bond rotation and vibration. Monatomic and homonuclear diatomic molecules cannot be detected since they do not have a net dipole moment. 5 SLPM outlet gas is drawn through a heated line at 180 °C and passes through the Temet Gasmet<sup>TM</sup> CX4000 FTIR for analysis. The gas is irradiated by infrared radiation between 900 and 4200 cm<sup>-1</sup>.

## High Performance Liquid Chromatography (HPLC)

MNPZ is measured using a Dionex<sup>TM</sup> UltiMate<sup>TM</sup> 3000 reverse phase High Performance Liquid Chromatography unit with UV detection. The MNPZ peak (RT = 4.7 mins) overlaps the peak of N-formyl piperazine, NFPZ, (RT = 4.5 mins), and the 0.2 mins difference is too small to be separated. When the mixtures contain both MNPZ and NFPZ, only one peak can be seen. IC chromatography can detect NFPZ but not MNPZ. To quantify MNPZ by HPLC, the samples are diluted 50 times in DI water for measurement, and the NFPZ concentrations measured by cation IC are used to back-calculate and exclude the NFPZ peak area from the total peak area.

# Cation and Anion Chromatography

The instrument used for ion chromatography is a Dionex ICS6000. The eluent of cation IC is a methane sulfonic acid (MSA) aqueous solution, and the eluent of anion IC is a potassium hydroxide (KOH) aqueous solution. Cation IC uses an IonPac GC17 guard column and an IonPac CS17 analytical column. Anion IC uses an IonPac AG15 guard column and an IonPac AS15 analytical column. NO<sub>2</sub> prescrubber samples are gravimetrically diluted 100 times in DI water to measure nitrite, sulfite, sulfate, and thiosulfate by anion IC, and 10,000 times to measure sodium by cation IC.

# Results

#### **NO<sub>2</sub> Analyzers**

There are three NO<sub>2</sub> UV analyzers (0–20 ppm NO<sub>2</sub>) at the boiler header, absorber inlet, and absorber outlet to monitor the removal of NO<sub>2</sub>, NO<sub>2</sub> concentration entering the absorber, NO<sub>2</sub> absorption by PZ, and the NO<sub>2</sub> concentration leaving from the top of the absorber. NO<sub>2</sub> data are presented in Figures 4 and 5. In Figure 4, the analyzers were incorrectly calibrated and generated false readings. Despite this there were two evident step changes when thiosulfate and sulfite were pumped into the prescrubber on December 21 at 12:50 and 14:45, respectively. Flue gas ceased to be available on December 23 due to the freezing conditions.



Figure 4: NCCC campaign NO<sub>2</sub> concentrations in the flue gas at the boiler header, absorber inlet, and absorber outlet in December 2022 operation.

When the pilot plant was started again in February 2023, the analyzers were carefully zeroed during calibrations. According to the results shown in Figure 5, there is 2.5 ppm NO<sub>2</sub> in the flue gas, the NO<sub>2</sub> prescrubber controls the NO<sub>2</sub> entering the absorber at 0.5 ppm, and PZ absorbs 50% NO<sub>2</sub> making the NO<sub>2</sub> leaving the absorber approximately 0.2 ppm. The NO<sub>2</sub> prescrubber removal efficiencies are calculated by the differences between the boiler header and absorber inlet NO<sub>2</sub> concentrations. The amounts of NO<sub>2</sub> absorbed by PZ in the absorber are the differences between the absorber inlet and outlet. The analyzers are calibrated weekly with a 5 ppm span, which can be observed in the spiking in Figure 5. Unfortunately, the absorber inlet analyzer was offline for 2–3 weeks because an unknown source of oil leaked into the ductwork and the absorber inlet analyzer sampling line, compromising the all-important analyzer. for the absorber inlet.



Figure 5: NCCC campaign NO<sub>2</sub> concentrations in the flue gas at the boiler header, absorber inlet, and absorber outlet in the 2023 operation.

NO in an aerobic environment will undergo a third-order reaction (Equations 1 and 2) and generate NO<sub>2</sub>. The best-accepted  $k_1$  is presented in Equation 3. To establish whether the NO conversion into NO<sub>2</sub> entering the analyzers is significant, an estimate of NO oxidation is required for data reliability. Four positions are of most concern: ductwork from the prescrubber to the absorber, sampling line to the absorber inlet analyzer, ductwork from the boiler header to the prescrubber, and the sampling line to the boiler header analyzer. With the information listed in Table 1 and Equations 2 and 3, NO<sub>2</sub> generation in these four positions is calculated and presented in the final column of Table 1. Compared to 0.5–2.5 ppm NO<sub>2</sub>, the estimated generation of 0.001–0.01 ppm NO<sub>2</sub> is negligible.

$$2NO + O_2 \to 2NO_2 \tag{1}$$

$$-\frac{d[NO]}{dt} = 2k_1[NO]^2[O_2]$$
(2)

$$k_1 = 1200e^{\frac{(530\pm400)}{T}} (L^2 \text{mol}^{-2} \text{s}^{-1})$$
(3)

Positions	NO (ppm)	O <sub>2</sub> (%)	Spec Diameter (in)x Length (ft)	G	τ (sec)	T (°F)	NO <sub>2</sub> gen (ppm)
Ductwork: PreS-Abs	- 10	13	14x109 10x116	8000 lb/hr	5.5	110	0.001
Abs in sampling line			0.125x80	1 SLPM	11.6	55.5	0.004
Ductwork: Boiler-PreS			0.76x70	10 SLPM (assumption)	37.5	115	0.009
Boiler sampling line			0.125x20	1 SLPM	2.9	55.5	0.001

Table 1: NO oxidation in the ductwork and sampling lines

#### Sulfite and thiosulfate performance

Sulfite, thiosulfate, and sulfate concentrations are measured by anion IC and shown in Figures 6 and 8. Additionally, cumulative sulfur and sodium are tracked for mass balance and are indicators of the chemical addition timings. Sodium sulfite, sodium thiosulfate, and NaOH addition causes step changes in species concentrations and cumulative sulfur/sodium. Cumulative sulfur is the summation of sulfite, thiosulfate, and sulfate. Sulfite and thiosulfate will eventually degrade into sulfate and N-S compounds. If there is N-S compound formation, cumulative sulfur will not be constant between each dosing of sulfite and thiosulfate. So far, the formation of N-S compounds is negligible. Cumulative sodium is measured directly by cation IC, and the dosing of NaOH for pH control contributes to the increase of sodium in addition to sodium sulfite and sodium thiosulfate addition.

Sulfite concentration decreases rapidly due to the absorption of NO<sub>2</sub> and radical oxidation. In Figure 9, the sulfite degradation rate during operation is approximately 0.8 mol/hr, equivalent to continuous consumption of 6 ppm SO<sub>2</sub> in the flue gas (G = 8000 lb/hr). It is not clear if thiosulfate effectively reduces sulfite degradation because the amount of thiosulfate is relatively constant. Moreover, sulfite concentration gradually dropped to 0 during the shutdown, while there was almost no change in thiosulfate (Figure 7). The prescrubber was circulating the solvent during the shutdown, even in the presence of thiosulfate.

The correlation between NO<sub>2</sub> removal and sulfite concentration is plotted in Figure 10. 25 mmol/kg sulfite can only provide 73% removal; 90% removal requires 65 mmol/kg sulfite. This campaign requires more sulfite to achieve the same NO<sub>2</sub> removal as the previous two campaigns, which concluded that 25 mmol/kg sulfite could remove 90% NO<sub>2</sub>. It is possible that having a certain amount of SO<sub>2</sub> in the flue gas is necessary or that the accuracy of the NO<sub>2</sub> analyzers is debatable.



Figure 6: Sulfite, thiosulfate, sulfate, cumulative sulfur, and cumulative sodium concentration in the NCCC campaign operating in December 2022.



Figure 7: Sulfite and thiosulfate moles during the shutdown of the NCCC campaign



Figure 8: Sulfite, thiosulfate, sulfate, cumulative sulfur, and cumulative sodium concentration in the NCCC campaign operating in 2023.



Figure 9: Sulfite and thiosulfate moles in the NCCC campaign operating in 2023



Figure 10: Sulfite and NO<sub>2</sub> removal in the NCCC campaign operating in 2023

#### **NH<sub>3</sub> generation**

 $NH_3$  is a good indicator of oxidation because it is the final product of oxidation and is volatile, making it easily measured by FTIR. FTIR alternates between measuring the flue gas from the absorber outlet and the water wash outlet. The  $NH_3$  FTIR data from the absorber outlet are shown in Figures 11 and 12. In Figure 11,  $NH_3$  generation decreased when the  $NO_2$  prescrubber was turned on, suggesting that removing  $NO_2$  from the flue gas reduced amine oxidation. In Figure 12,  $NH_3$  generation is less when the  $NO_2$  removal efficiency is higher.



Figure 11: NH<sub>3</sub> concentration in the flue gas leaving from the absorber outlet in the NCCC campaign operating in December 2022



Figure 12: NH<sub>3</sub> concentration in the flue gas leaving the absorber outlet in the NCCC campaign operating in 2023

#### **Precipitation in the NO<sub>2</sub> Prescrubber**

Some NO<sub>2</sub> prescrubber samples have yellow precipitate (Figure 13), but the textures differ, suggesting that there might be more than one component. 179A in Figure 13 is the same sample as 179B but with formaldehyde addition. 179 A has precipitate but 179 B has none. Hence, formaldehyde caused the precipitation that the precipitate solubility is lower in formaldehyde solution. The precipitate is initially speculated to be a mixture of sulfur, sodium sulfate, and sodium bicarbonate for the following reasons: (1) Precipitate disappeared, and the amount of thiosulfate increased (Figure 8) after sulfite addition. Hence, reaction  $S + SO_3^{2-} \rightarrow S_2O_3^{2-}$  might happen. (2) Three phase equilibrium of ternary systems exist in the prescrubber: Na<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>3</sub>-H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>4</sub>-NaHCO<sub>3</sub>-H<sub>2</sub>O. The prescrubber temperature is approximately 315 K. The concentration of Na<sub>2</sub>SO<sub>4</sub> is 0–2.75 M, the maximum concentrations of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> are 3.7 M (334 K) and 1.3 M (320 K), respectively (Zhu, 2015). At room temperature, the solubility of Na<sub>2</sub>SO<sub>4</sub> is 1.98 M, Na<sub>2</sub>CO<sub>3</sub> is 3.2 M, and NaHCO<sub>3</sub> is 1.14 M. Based on the above, Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub> are more likely to precipitate.

When the pH setpoint was 9.0, the CO<sub>2</sub> concentration was 0.3 mol/kg measured by TIC, which is high, although it was not on the edge of precipitation. As a result, the set point of pH of the prescrubber was strategically reduced to suppress CO<sub>2</sub> absorption for a lower  $HCO_3^-$  generation. However, the pH became unstable after the setpoint was stepped down to 8.5 because lower  $[HCO_3^-]$  provided less buffering effect, as seen in Figure 14.

Comparing the one-day pH and tank level data for March 2 and 7 in Figures 15 and 16, there should be a buffer point for the prescrubber between 8.5 and 9.0, which is the suggested setpoint to achieve pH stability and lower  $[HCO_3^-]$  at the same time. CO<sub>2</sub> and NO<sub>2</sub> absorption made the pH drop after sulfite was added, while the generation of the N-S compounds raised the pH (Figure 3). Tank level indicates whether NaOH was added to raise the pH. After sulfite was added, the

pH dropped only to 7.8 before increasing to 8.8 without NaOH addition on March 2, and the pH dropped significantly to 6.5 on March 7. The initial pH when sulfite was added made the difference, which was 8.8 on March 2 and 8.5 on March 7. Therefore, there was more  $[HCO_3^-]$  on March 2 to provide a better buffering effect than on March 7.

Sodium accumulation, as well as the precipitation of Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub>, is undesirable. The sodium will increase as sodium sulfite, sodium thiosulfate, and sodium hydroxide are added to maintain NO<sub>2</sub> prescrubber performance. The most direct way to simultaneously control Na<sub>2</sub>SO<sub>4</sub> and sodium accumulation onsite is to maintain a liquid density of less than 68.5 lb/ft<sup>3</sup>. However, when the addition of salt and water increases the surge tank level above 80%, solution must be discharged to disposal. This will waste sulfite and thiosulfate while dumping sulfate and sodium. The density data are in Figure 17. Figure 18 shows that the tank level has been increasing due to the demand for pH adjustment, chemical addition, and density control.



Figure 14: pH of the NO<sub>2</sub> prescrubber; blue dots indicate the timing of sulfite addition.



Figure 15: pH of the NO<sub>2</sub> prescrubber on March 2; the orange dot indicates the timing of sulfite addition.



Figure 16: pH of the NO<sub>2</sub> prescrubber on March 7; the orange dot indicates the timing of sulfite addition.



Figure 17: Liquid density of the NO<sub>2</sub> prescrubber; orange dots indicate the timing of sulfite addition.



Figure 18: Tank level of the NO<sub>2</sub> prescrubber; orange dots indicate the timing of sulfite addition.

#### **MNPZ** concentrations

MNPZ comes from the reaction of PZ and nitrite, which is the stoichiometric product of the NO<sub>2</sub> absorption by PZ. MNPZ forms instantly but is not thermally stable. Both the formation and degradation rates of MNPZ are sensitive to temperature with positive activation energies. All the nitrite will be completely converted into MNPZ when the solvent passes through the high temperature parts of the system, especially the stripper sump, which has the highest temperature with a long residence time. Meanwhile, the first-order degradation reaction of MNPZ becomes faster as the MNPZ accumulates in the system. Eventually, MNPZ will reach a steady-state concentration, determined by the NO<sub>2</sub> concentration in the flue gas, absorption efficiency of NO<sub>2</sub> by PZ, flue gas flow rate, and the stripper sump temperature and volume, as described in Equation 4. Equation 4estimatse the steady-state concentration and back-calculates the amount of NO<sub>2</sub> absorbed by PZ using the measured MNPZ steady-state concentration.

$$[NO_2] \times \eta \times G = [MNPZ]_{ss} \times k_{decomp} \times V_{sump}$$
(4)

$$k_{decomposition}(T) = 10.4 \times 10^{-6} \exp(\frac{-94 \, kJ}{R} \left(\frac{1}{T} - \frac{1}{408}\right)) \tag{5}$$

where:

[ $NO_2$ ]: NO<sub>2</sub> concentration in the flue gas;  $\eta$ : absorption efficiency of NO<sub>2</sub> by PZ; G: flue gas flow rate; [MNPZ]<sub>ss</sub>: MNPZ steady-state concentration;  $k_{decomp}$ : MNPZ decomposition rate constant;  $V_{sump}$ : Stripper sump temperature.

Figure 19 shows the MNPZ concentrations measured by HPLC. The accumulation of MNPZ was stopped by turning on the NO<sub>2</sub> prescrubber on December 21, 2022. During the shutdown, there was no decrease in MNPZ concentration (Table 2) since the entire unit was exposed to the ambient environment with no high temperature exposure. Before the pilot plant was started again in February, fresh PZ was added to the unit and that diluted MNPZ concentration to 1.5 mmol/kg. With the NO<sub>2</sub> prescrubber, NO<sub>2</sub> entering the absorber is controlled at 0.5 ppm, and MNPZ gradually reaches a steady state of 2 mmol/kg. Through back calculation, the 2 mmol/kg steady-state MNPZ concentration implies that PZ absorbed 0.25 ppm NO<sub>2</sub> in the flue gas. This 50% NO<sub>2</sub> absorption is at the same scale as the 2022 SRP pilot plant, which achieved 43% NO<sub>2</sub> absorption by PZ.



Figure 19: MNPZ concentrations of NCCC campaign operation since December 2022

Date	MNPZ (mmol/kg)	Site	
12/22/22 08:30	2.3	rich	
1/4/23 13:10	2.3	401 Tank	
1/10/23 09:25	2.2	rich	

Table 2: MNPZ concentration during the shutdown

#### Conclusions

- 1. There is no SO<sub>2</sub> in the flue gas for this NCCC campaign. Therefore, sulfite is added intermittently to control NO<sub>2</sub> concentration entering the absorber lower than 0.5 ppm. To date, 125 lb of sodium sulfite is added per week.
- 2. NO<sub>2</sub> concentration in the boiler flue gas is 2.5 ppm. The sulfite/thiosulfate prescrubbing method can control the NO<sub>2</sub> concentration down to 0.5 ppm. PZ absorbs 50% of the NO<sub>2</sub> in the absorber, leaving 0.25 ppm NO<sub>2</sub> vented from the absorber top.
- 3. The NO<sub>2</sub> analyzers are calibrated weekly using a 5 ppm span.
- 4. The interference of NO oxidation to NO<sub>2</sub> analysis is negligible.
- 5. To achieve 90% NO<sub>2</sub> removal, 65 mmol/kg sulfite is required in this campaign.
- 6. The degradation rate of sulfite in the NO<sub>2</sub> prescrubber is about 0.8 mol/hr, equivalent to consuming 6 ppm SO<sub>2</sub> in the flue gas.

- 7. It is unclear if thiosulfate inhibits oxidation because thiosulfate is held relatively constant compared to sulfite. If thiosulfate plays its role in protecting sulfite, the total amount of thiosulfate is expected to decrease.
- 8. Sulfite concentration dropped to near zero during the shutdown, while there was almost no change in thiosulfate. This result suggests an oxidation pathway oxidized sulfite that thiosulfate could not stop.
- 9. The generation of N-S compounds is negligible.
- 10. NH<sub>3</sub> generation is lower when the NO<sub>2</sub> removal is higher.
- 11. The precipitate in the NO<sub>2</sub> prescrubber might be a mixture of sulfur, sodium sulfate, and sodium bicarbonate. The addition of sulfite dissolves the precipitate, while the formaldehyde makes the precipitation occur.
- 12. The attempts to control precipitation include pH control for lower  $[HCO_3^-]$ , and density control for lower  $[Na_2SO_4]$  and  $[Na^+]$ . When the  $[Na_2SO_4]$  is about to exceed 2 M, or the tank level reaches a level > 80%, bleeding will be necessary instead of adding water.
- 13. The suggested pH setpoint is 8.5–9.0. pH higher than 9.0 increases CO<sub>2</sub> absorption and HCO<sub>3</sub><sup>-</sup> generation. The system will have less [HCO<sub>3</sub><sup>-</sup>] to provide a good buffering effect if the pH is lower than 8.5.
- 14. MNPZ concentration has reached its steady state of 2 mmol/kg with 0.5 ppm NO<sub>2</sub> entering the absorber and 50% NO<sub>2</sub> absorption efficiency by PZ.

## Future work

- 1. RTI solvent in HGF reactor to test the NO<sub>2</sub> oxidation.
- 2. Quantify OPZ concentration on LCMS-TOF.

### References

Fine NA. *Nitrosamine Management in Aqueous Amines for Post-Combustion Carbon Capture*. The University of Texas at Austin. Ph.D. Dissertation. 2015.

Moser P, Wiechers G, Schmidt S, Figueiredo R, Skylogianni E, and Monteiro J. "Conclusions from 3 years of continuous capture plant operation without exchange of the AMP/PZ-based solvent at Niederaussem – Insights into solvent degradation management." *16th International* 

Conference on Greenhouse Gas Control Technologies GHGT-16, 23–27<sup>th</sup> October, 2022, Lyon, France.

- Nielsen PT. Oxidation of Piperazine in Post-Combustion Carbon Capture. The University of Texas at Austin. Ph.D. Dissertation. 2018.
- Voice AK. Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing. The University of Texas at Austin. Ph.D. Dissertation. 2013.
- Wan X, Luo M, Chen H, and Song X. "Phase Equilibrium of the Ternary System Na2SO3–Na2SO4–H2O at 293.15, 313.15, and 353.15 K." J. Chem. Eng. Data 2022;67(10):3201–3209.
- Zhu WY, Gu Y, Zhang L, Jing H, Liu B, Zhang FB, Zhang GL, and Xia Q. "Solubility of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> in Aqueous Sodium Sulfate Solutions and Its Application to Separating Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> Salt Mixtures." *Ind. Eng. Chem. Res.* 2015;54(19):5345–5348.