

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 63 (2014) 830 – 847

Energy
Procedia

GHGT-12

Absorption of nitrogen oxides in aqueous amines

Nathan A. Fine^a, Gary T. Rochelle^{a*}^aThe University of Texas at Austin, Department of Chemical Engineering, 200 E Dean Keeton St. Stop C0400, Austin, TX 78712-1589**Abstract**

Nitric oxide (NO) and nitrogen dioxide (NO₂) were absorbed into aqueous amine to determine the absorbing species, the absorption kinetics, and the aqueous products at the ppm-level NO_x concentrations typical of flue gas from fossil fuel power plants. At flue gas conditions of 0.5-5 ppm of NO₂, absorption is dominated by free radical absorption of NO₂ as nitrite. NO₂ absorption kinetics are first order in NO₂ partial pressure, half order in free amine concentration, and fastest in methyldiethanolamine (MDEA). The reaction-enhanced liquid mass transfer coefficient for NO₂ absorption in 8 m piperazine (PZ) at absorber conditions is 9.7×10^{-7} mol/s·m²·Pa, yielding 92% NO₂ absorption at a typical A/G of 3.3×10^6 s·Pa·m²/mol. Similarly, a 9 m monoethanolamine (MEA) solvent will absorb roughly 70% of the inlet NO₂ while a 7 m MDEA/2 m PZ solvent will absorb over 99% of the NO₂. Nitrite and nitrate are the main NO_x absorption products in MDEA with nitrite dominating at low NO₂ partial pressures. In PZ, the amine free radical formed during NO₂ absorption will react with NO to directly form n-nitrosopiperazine (MNPZ) or react with itself to form 2-piperazolinol (2-PZOH). Typical nitrosamine yields in 5 m PZ are around 15% of total absorbed NO_x and can be halved with the addition of 200 mM Inhibitor A, a free radical scavenger. Nitrate and nitramine are minor products of NO_x absorption, accounting for less than 5% of total absorbed NO_x.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: nitrosamine; NO_x absorption; amine scrubbing; nitrite

* Corresponding author. Tel.: +1-512-471-7230; fax: +1-512-471-7060

E-mail address: gtr@che.utexas.edu

1. Introduction

1.1 Nitrosamine accumulation in amine scrubbing

Amine scrubbing is an efficient and proven method for carbon capture, but as a chemical process, it has the potential to form toxic byproducts such as nitrosamines [1,2]. Figure 1 gives a proposed sequence of processes that determine nitrosamine accumulation in amine scrubbing. Flue gas containing nitrogen oxides (NO_x) enters a polishing scrubber where a fraction (A) of the NO_x can be removed via reaction with sulfite or tertiary amine [3–5]. The remaining NO_x then enters the absorber where a portion of the nitrogen dioxide (NO₂) can absorb into the amine solution as nitrite (β). The NO can also absorb into solution via reaction with the amine radical to directly form the nitrosamine (γ) [6,7]. The rest of the NO_x will vent from the absorber along with the scrubbed flue gas. Amine oxidation is another source of nitrite in amine solvents that are not oxidatively stable such as monoethanolamine (MEA) [8,9]. Nitrite from NO_x absorption and amine oxidation will then travel to the stripper where it can nitrosate a secondary amine with a yield of δ. The yield is determined by the concentration of secondary amines in the solvent and their relative nitrosation rates compared to the principal amine [10,11]. After nitrosation, the nitrosamine will thermally decompose in the stripper sump according to a pseudo-first-order nitrosamine decomposition rate constant (k_{str}) [12,13]. Nitrosamine sources from NO_x absorption and amine oxidation will balance out with nitrosamine thermal decomposition to yield a steady-state nitrosamine concentration (Equation 1). This work focuses on NO_x absorption into aqueous amines, which is important for NO_x removal in the polishing scrubber (A) and NO_x absorption in the absorber (β and γ).

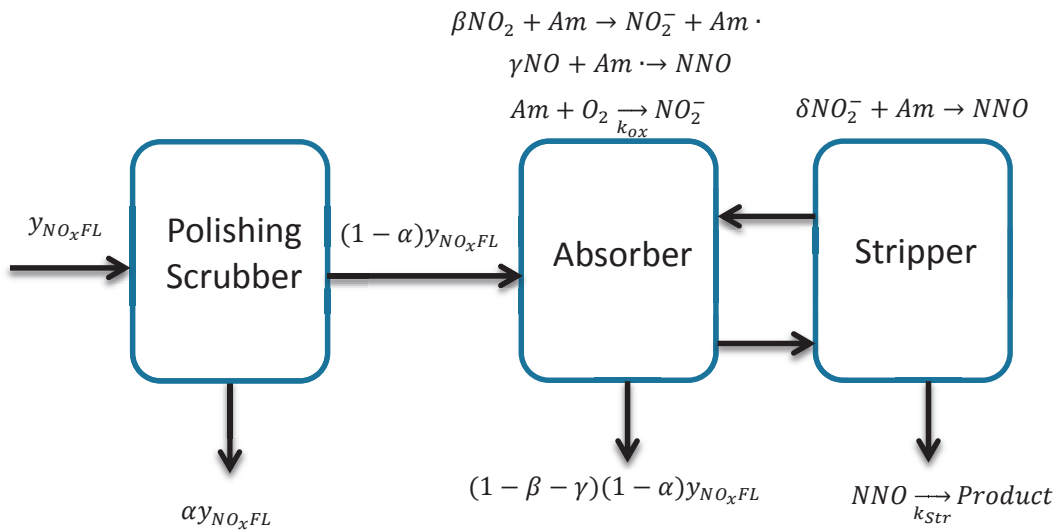


Figure 1: Nitrosamine Accumulation in Amine Scrubbing

$$NNO \text{ Steady State} = \frac{(1 - A)y_{NO_x} \frac{G}{L} (\delta\beta + \gamma) + \delta k_{ox} \tau_{Tot}}{k_{Str} \tau_{Str}} \tag{1}$$

1.2 NO_x absorption into aqueous solutions

NO_x absorption at high concentrations has been heavily studied for the manufacturing of nitric acid [14]. With NO_x concentrations at approximately 10% by volume, NO_x absorption is dominated by the molecular absorption of dinitrogen trioxide (N₂O₃), and dinitrogen tetraoxide (N₂O₄). Absorption of N₂O₄ is pH independent above a pH of 5 since the pK_a of HNO₃ is low enough that it is completely dissociated in solution. However, the absorption of N₂O₃ depends on basicity due to the speciation of HNO₂ in the boundary layer. The fastest absorption rates are above a pH of 7 where HNO₂ is also completely dissociated in the boundary layer [15]. The equilibria for N₂O₃ and N₂O₄ are both second order in NO_x. Thus as NO_x concentration decreases, N₂O₃ and N₂O₄ comprise a decreasing proportion of the total NO_x. Even after accounting for the greater solubility of N₂O₃ and N₂O₄, only 0.2% of total absorbed NO_x at the gas-liquid interface exists as N₂O₃ or N₂O₄ at flue gas conditions compared to 66% during nitric acid manufacturing (Table 1).

Table 1: NO_x speciation under nitric acid manufacturing and flue gas conditions T = 25 °C, P = 1 Bar
Equilibria and Henry's coefficients from Patwardhan et al. [15]

Species	Henry's constant (M/Pa)	Concentration in equilibrium with 10% NO _x , 0.5% NO ₂ (M)	Concentration in equilibrium with 100 ppm NO _x , 5 ppm NO ₂ (M)
NO	1.84E-08	1.7E-04	3.6E-08
NO ₂	1.18E-07	2.9E-05	1.7E-07
N ₂ O ₃	5.92E-06	1.5E-04	1.5E-10
N ₂ O ₄	1.38E-05	2.3E-04	2.3E-10

Due to the low concentration of N₂O₃ and N₂O₄, research for NO_x absorption at flue gas conditions has focused on the free radical absorption of NO₂. Sulfite, bisulfite, and sulfide all absorb NO₂ directly, greatly enhancing absorption at low NO_x levels [3,5]. Amines also enhance NO_x absorption with tertiary amines offering the highest absorption rates [4]. Nitrosamines have been shown to form during NO_x absorption into amine solutions at alkaline conditions [7,16–18]. At high NO_x concentrations, this can be attributed to the absorption of N₂O₃ and N₂O₄, two strong nitrosating agents [19]. However, Challis et al. theorize that at low NO_x concentrations and low amine concentrations, nitrosation is more likely to occur through free radical absorption of NO₂ followed by amine radical reaction of NO (Figure 2).

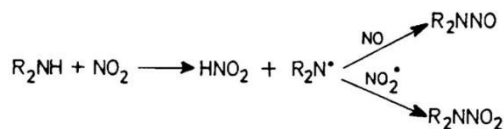


Figure 2: Series reaction to form nitrosamine [7]

2. Experimental Methods

2.1 Wetted Wall Column Apparatus

The mass transfer of NO₂ into amine solutions was measured using the wetted wall column (WWC) previously described by Dugas [20]. Briefly, a hydrated gas containing NO₂ contacts an amine solution over a known surface area. NO₂ concentration at the inlet and outlet of the wetted wall column are measured using a hot-gas FTIR [9]. The reaction enhanced liquid mass transfer coefficient (k_g') can then be

determined using the rate-based equation for NO₂ flux with a log mean partial pressure driving force (Equations 2-4).

$$N_{NO_2} = K_g * P_{NO_2 LM} = \frac{G_{WWC} * (y_{NO_2 in} - y_{NO_2 out})}{A_{WWC}} \quad (2)$$

$$P_{NO_2 LM} = \frac{P_{NO_2 in} - P_{NO_2 out}}{\ln\left(\frac{P_{NO_2 in}}{P_{NO_2 out}}\right)} \quad (3)$$

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{k_g'} \quad (4)$$

Conditions for the inlet gas stream are shown below (Table 2). The total solvent inventory for the WWC is approximately 2 L, which allows for lengthy experiment times without appreciable accumulation of absorption products that might interfere with rate measurements.

Table 2: WWC Gas Stream Conditions

Condition	Range
Temperature (°C)	20–40
Pressure (psig)	20–40
Flow Rate (SLPM)	2–7
NO ₂ (ppm)	50–300
H ₂ O (%)	2.3–7.4
CO ₂ (%)	0–4
N ₂ (%)	76–98

2.2 High Gas Flow Apparatus

The WWC is ill-suited to measure aqueous products from NO_x absorption because of its large inventory, so the high gas flow contactor (HGF) previously described by Sexton [8] was repurposed to measure the reaction products of NO_x absorption. Briefly, a hydrated gas containing NO_x is sparged through 0.35 L of amine solvent (Table 3). NO_x concentration at the inlet and outlet of the HGF are measured using a hot-gas FTIR. The liquid is sampled by first setting the gas to bypass and then withdrawing 1 mL of sample through a septum. Absorption yields are determined by comparing reaction products to the overall mass balance of absorbed NO_x (Equation 5).

Table 3: HGF Gas Stream Conditions

Condition	Range
Temperature (°C)	20–60
Pressure	Atmospheric
Flow Rate (SLPM)	7.5
NO ₂ (ppm)	10–150
NO (ppm)	0–100
H ₂ O (%)	2–20
CO ₂ (%)	0.5–6
N ₂ or Air (%)	74–98

$$[NO_{2 Abs}] = \frac{P G_{HGF}}{RT} * m_{sol} * (y_{NO_2 in} - y_{NO_2})t \quad (5)$$

2.3 Aqueous Sample Analysis

Amines are analyzed using cation chromatography as described by Namjoshi et al. [21]. Nitrite and nitrate are analyzed using anion chromatography as described by Nielsen et al. [22]. N-nitrosopiperazine (MNPZ) is analyzed using high pressure liquid chromatography [12] and 2-piperazinol (2-PZOH) is analyzed using a dinitrophenylhydrazine (DNPH) derivitization method [13].

3. Results

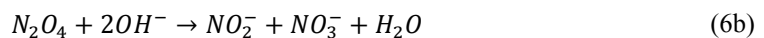
Table 4 gives all the results for wetted wall column experiments. NO₂ absorption is modeled as a fast reaction in the liquid boundary layer with the pseudo-first-order assumption. NO₂ hydrolysis is assumed to be second order in NO₂ partial pressure while NO₂ absorption in amine is assumed to be first order.

Table 4: NO₂ absorption kinetics in the WWC

Solution	CO ₂ Loading	T (°C)	k _g '*10 ⁷ (mol m ⁻² s ⁻¹ Pa ⁻¹)
0.001 M NaOH	0	20	0.13√P _{NO₂}
0.001 M NaOH	0	40	0.11√P _{NO₂}
5 m MEA	0.48	20	1.6
5 m MEA	0.48	40	1.9
9 m MEA	0.38	40	3.0
9 m MEA	0.48	20	1.9
9 m MEA	0.48	40	2.0
8 m PZ	0.26	40	13.7
8 m PZ	0.32	20	7.2
8 m PZ	0.32	40	9.7
8 m PZ	0.39	40	8.0
0.40 m MDEA	0	20	36.9
0.40 m MDEA	0	40	41.3
0.056 m MDEA	0	20	11.8
0.056 m MDEA	0	40	22.7
0.023 m MDEA	0	20	7.5
0.023 m MDEA	0	40	9.7

3.1 NO₂ Hydrolysis

Under basic conditions NO₂ absorbs into water as (N₂O₄), which then forms nitrite and nitrate (Equations 6a & 6b). Using film theory, the solution for NO₂ flux is given by Equation 7. Gas side mass transfer resistance can be ignored due to the relatively slow reaction kinetics.



$$N_{NO_2} = P_{NO_2} \sqrt{\frac{2k_{H_2O} D_{N_2O_4} P_{NO_2}}{3H_{N_2O_4}^2}} = C_1 * P_{NO_2}^{3/2} = k'_g * P_{NO_2} \quad (7)$$

The flux of NO_2 into 0.001 M NaOH was measured from 2–30 Pa NO_2 at 20 °C and 40 °C. Flux as a function of NO_2 partial pressure was regressed using Equation 7 with C_1 as a free parameter. The data agrees well with the literature even though the experiments were run at different partial pressures and on different apparatuses (Figure 3). The experiment was attempted at 60 °C, but the results drastically over-predicted k_g' . This is most likely due to water condensation in the lines directly after the WWC, which provides extra surface area for NO_2 absorption.

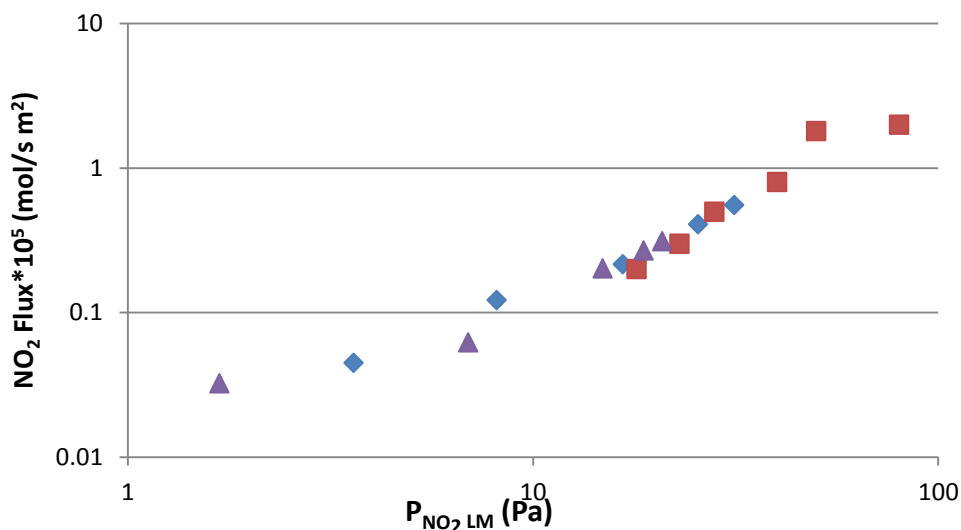


Figure 3: NO_2 Hydrolysis on the WWC at 20 °C (blue diamonds) and 40 °C (purple triangles) compared to NO_2 hydrolysis using the stirred cell at 25 °C [3] (red squares)

3.2 NO_2 Absorption into Amines during CO_2 Capture

NO_2 flux was measured in the wetted wall column at partial pressures ranging from 1–15 Pa. The gas side mass transfer coefficient (k_g) was measured with NO_2 absorption into 5.8 m methyldiethanolamine (MDEA), which has negligible liquid mass transfer resistance. The value for k_g is $25.2 \cdot 10^7 \frac{\text{mol}}{\text{m}^2 \text{ s Pa}}$, approximately 40% higher than the k_g predicted for the wetted wall column under these conditions [23,24]. NO_2 flux into amine solutions is linear with respect to NO_2 partial pressure and passes through zero, suggesting that NO_2 absorption is dominated by first-order free radical absorption under experimental conditions (Figure 4).

The free radical absorption of NO_2 as nitrite is hypothesized to be first order in free amine, leading to a half-order amine dependence for the liquid mass transfer coefficient (Equation 8).

$$k_g' = \sqrt{\frac{k_{Am}[Am]_{Free}D_{NO_2}}{H_{NO_2}^2}} \quad (8)$$

The k_g' for NO_2 absorption into dilute MDEA is approximately half-order in total MDEA as hypothesized, and k_g' also increases with increasing free amine in piperazine (PZ) and MEA (Figure 5). However, k_g' flattens out at higher PZ loadings, suggesting that other PZ species such as PZH^+ and PZCOO^- could also absorb NO_2 . Finally, k_g' increases with increasing order of amines similar to the free radical absorption of ClO_2 in amines [2].

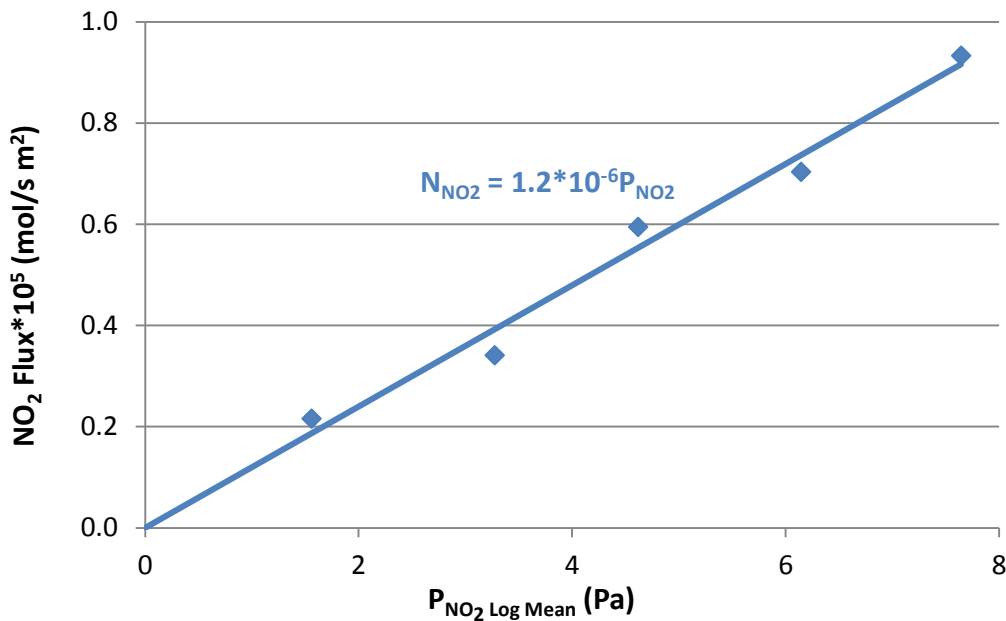


Figure 4: NO₂ Absorption into 0.05 m MDEA at 20 °C

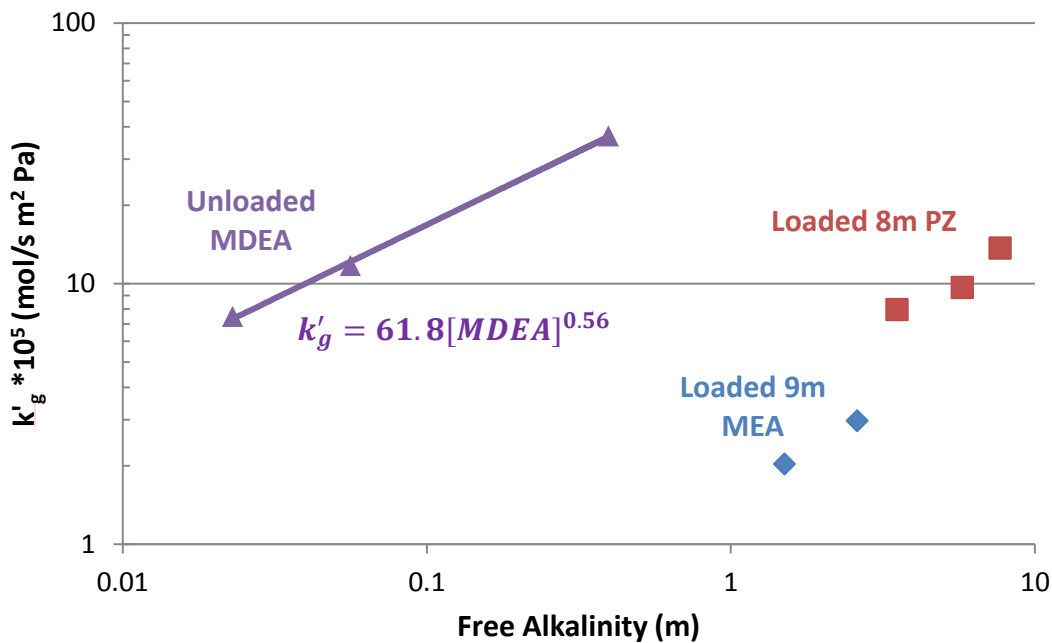


Figure 5: Dependence of k'_g on amine order and amine concentration, T = 40 °C

The fraction of NO₂ absorbed during CO₂ scrubbing can be estimated from the mass transfer coefficients and total wetted area of a typical amine scrubber (Equations 9 & 10). A typical MEA absorber designed for 90% CO₂ capture will absorb roughly 70% of inlet NO₂, PZ will absorb roughly 90% and MDEA/PZ will absorb over 99%. NO₂ hydrolysis can only account for 4% of total NO_x absorption (Table 5).

$$\frac{NO_2 \text{ absorbed}}{NO_2 \text{ Flue}} = (1 - e^{-N_{OG}}) \quad (9)$$

$$N_{OG} = \frac{K_G * A}{G} \quad (10)$$

Table 5: NO₂ absorbed in typical amine scrubbers

Solvent	A/G (m ² s Pa/mol)	K _g (mol/m ² s Pa)	NO ₂ Absorbed (%)
9 m MEA	4.3*10 ⁶	3.0*10 ⁻⁷	73
8 m PZ	2.6*10 ⁶	9.7*10 ⁻⁷	92
7 m MDEA/2 m PZ	2.6*10 ⁶	k _g limited	>99
Water at 2 ppm NO ₂	2.6*10 ⁶	0.16*10 ⁻⁷	4

3.3 NO_x Absorption into MDEA

Tertiary amines are promising candidates for scrubbing NO₂ in a polishing scrubber before it reaches the absorber. Since NO does not absorb into solution by itself, one needs only to scrub the NO₂ to reduce the available nitrite, and ultimately reduce nitrosamine accumulation. Given a polishing scrubber with an A/G of 1.0*10⁶ s·Pa·m²/mol, 90% NO₂ absorption could be achieved with k_g' = 23.0*10⁻⁵ mol/s·Pa·m². Figure 5 shows that this could be achieved with 0.17 m free MDEA in the polishing scrubber. Previously, sodium sulfite was studied for scrubbing NO₂ from flue gas. However, in aerobic environments sulfite catalytically oxidizes, drastically decreasing free sulfite in the boundary layer. The oxidation can decrease the rate of NO₂ absorption by 40% compared to an oxygen-free environment, necessitating the use of oxidation inhibitors [3]. In comparison, tertiary amines are oxidatively stable at low temperatures, so there is no expected penalty for NO_x absorption in a relatively high oxygen environment.

Hydrated N₂ gas with 60 ppm NO₂ was absorbed into a solution of 0.1 m MDEA at 20 °C for 2 hours using the HGF. The samples were extracted periodically and analyzed for nitrite and nitrate using anion chromatography. Nitrite and nitrate increased linearly with absorbed NO₂ (Figure 6) and together accounted for all of the absorbed NO₂. The same samples were analyzed for MDEA and methylaminoethanol (MAE) using cation chromatography. MDEA decomposition was not catalyzed by NO₂ absorption in the anaerobic environment with only 1.1 moles of MDEA decomposing for every mole of NO₂ absorbed. MAE is the only quantified amine product from NO₂ absorption, accounting for 67% of the decomposed MDEA (Figure 7). The experiment was repeated with air as the diluent and metal catalysts added to the amine solution, but there was no change in NO_x absorption products or MDEA decomposition rate.

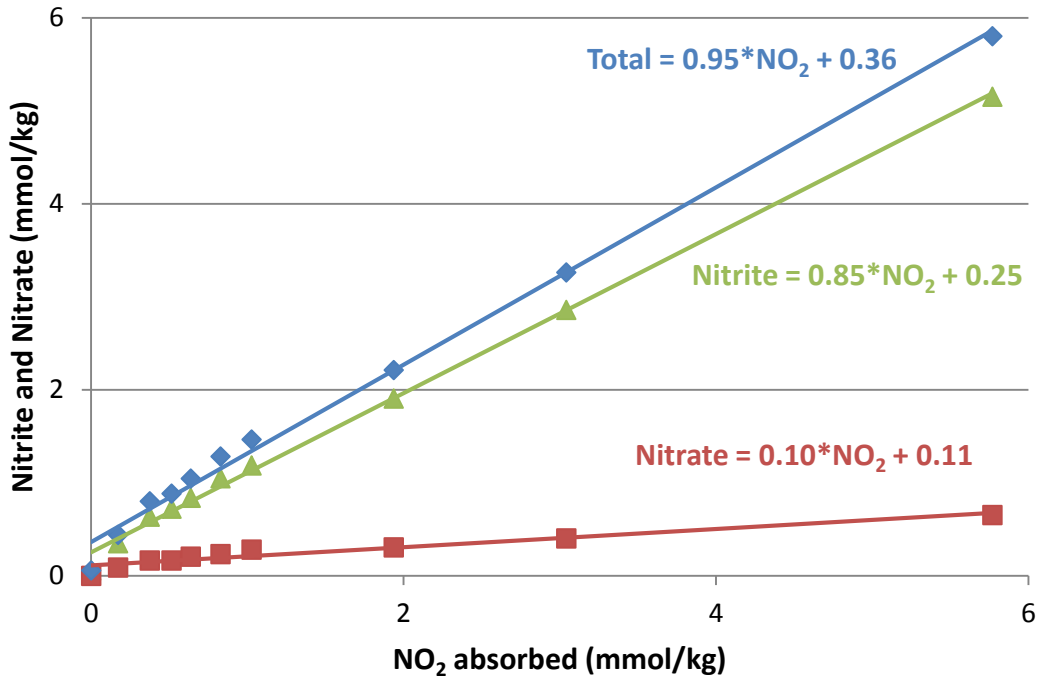


Figure 6: Nitrite and nitrate from NO₂ absorption into 0.1 m MDEA with 60 ppm NO₂ in hydrated N₂; T = 20 °C.

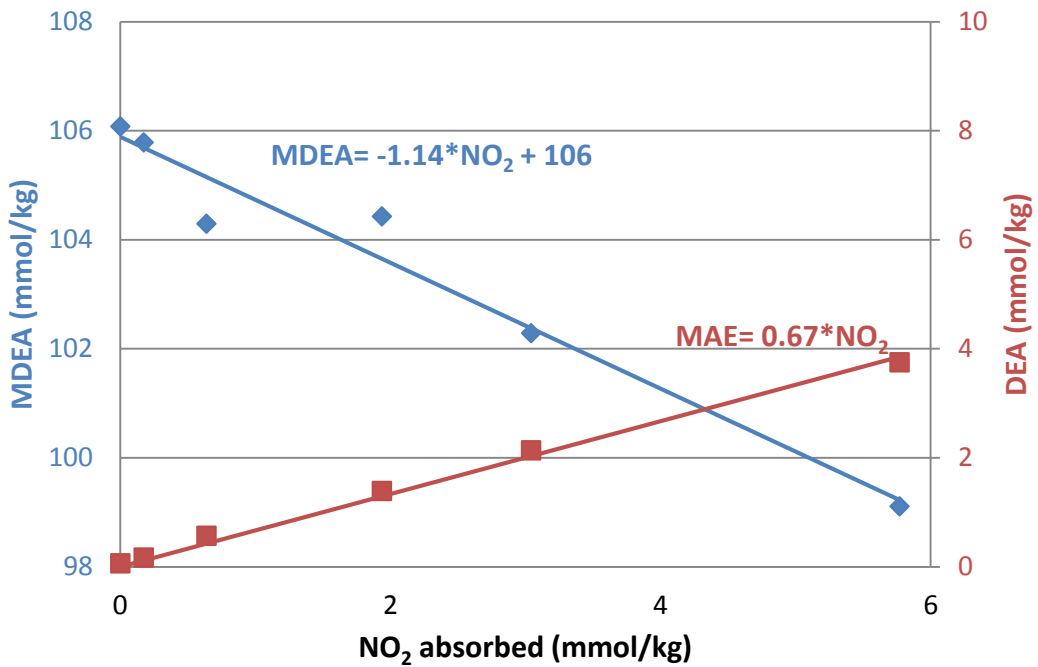


Figure 7: Amine products from NO₂ absorption into 0.1 m MDEA with 60 ppm NO₂ in hydrated N₂; T = 20 °C.

For a set of experiments NO_2 partial pressure was allowed to vary from 4 ppm to 144 ppm. Absorption products increased linearly with absorbed NO_2 , and the data was linearly regressed with the slope representing the yield. The mole balance closed with an average of 97% of the total absorbed NO_x accounted for in the aqueous phase. Thus nitrosamine formed in MDEA could account for at most 3% of total absorbed product. Under similar conditions, Dai et al. reported that less than 1% of NO_x absorbed in MDEA formed nitrosamine [16]. At very low concentrations of NO_2 almost all of the NO_2 absorbed as nitrite, which is consistent with free radical absorption of NO_2 . As the concentration of NO_2 increased, the yield to nitrate increased, which shows the growing importance of NO_2 hydrolysis at high NO_2 concentrations (Figure 8). Both NO and oxygen had very little effect on the overall absorption products, proving that N_2O_3 is not an important absorption species under experimental conditions. A similar result with nitrite yield unaffected by NO concentration was obtained by Dai et al. in morpholine solution [25].

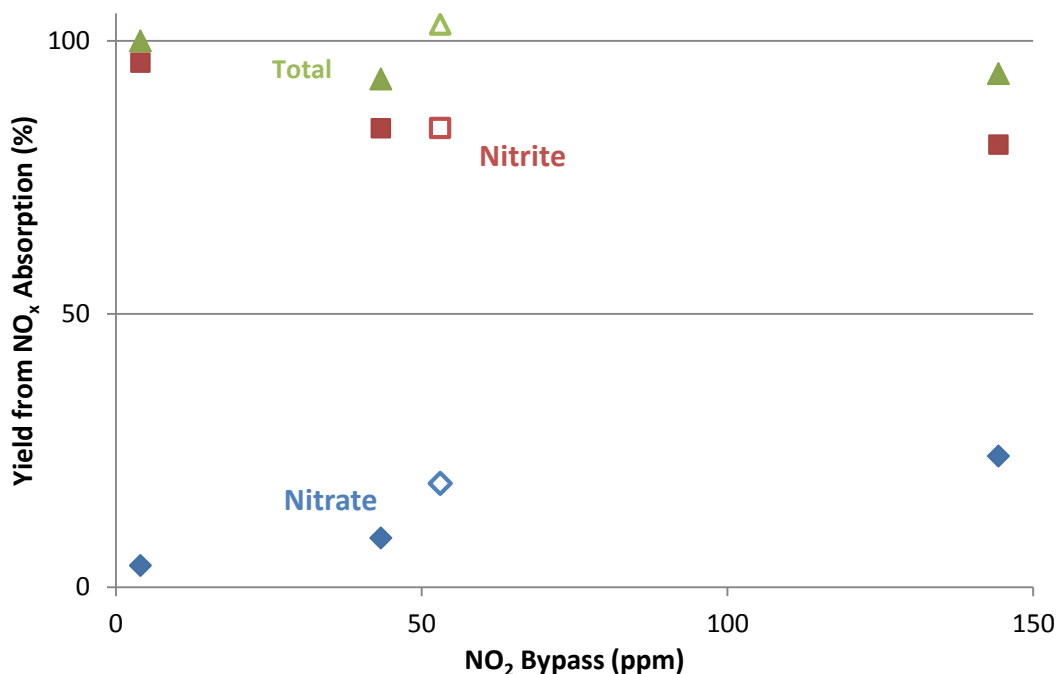


Figure 8: Nitrate and nitrite in 0.1 m MDEA, $T = 20\text{ }^\circ\text{C}$ (Closed points: NO_2 in N_2 ; Open Points: NO_2 with 200 ppm NO in air).

3.4 NO_x absorption into unloaded 1 m PZ

Unlike the radicals formed during NO_2 absorption in MDEA, the PZ radical can directly react with NO to form a stable nitrosamine. Previous research has shown that secondary amines will yield the highest nitrosamine concentrations during NO_x absorption [16] with nitrosamine yields of $6\pm 2\%$ of total absorbed NO_x in PZ at absorber conditions. The HGF was again used to study NO_x absorption products in 1 m PZ at $20\text{ }^\circ\text{C}$. All experiments were performed with 100 ppm NO and NO_2 varying from 10 to 100 ppm. MNPZ, nitrite, and nitrate were all proportional to total absorbed NO_x and together closed the mole balance within 4% (Figure 9). Nitrosamine yield varied from 20% to 35% of the total absorbed NO_x with no dependence on oxygen in the gas (Figure 10). Nitrosamine yield decreases with increasing NO_2 partial pressure, most likely due to the free radical termination step. At high concentrations of NO_2 , there are more free radicals formed in the boundary layer. These can react with each other to form 2-PZOH with a second-order

dependence on free radical concentration (Equation 11). As the NO_2 partial pressure decreases, the free radical concentration decreases, and the radical is more likely to terminate by reacting with NO to yield MNPZ (Equation 12). The free radicals may also react with NO_2 to form the nitramine (Equation 13). However, nitramine concentration has been shown to be much lower than nitrosamine concentration [26] because NO_2 reacts quickly with the amine and is thus at a much lower concentration throughout the reaction boundary layer.

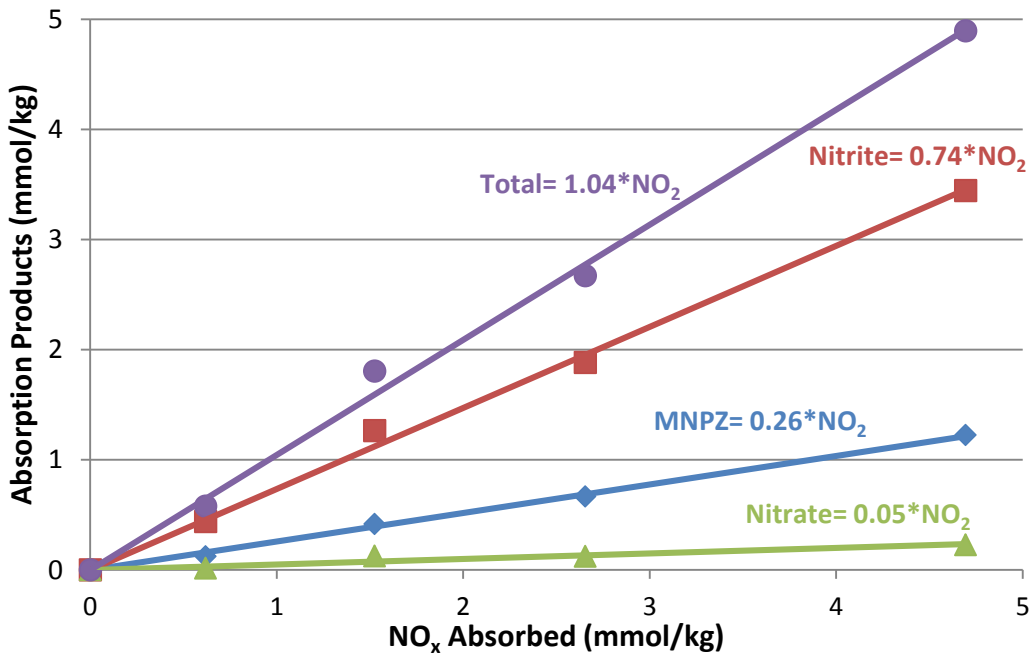


Figure 9: NO_x absorption products in 1 m PZ with 40 ppm NO_2 , 100 ppm NO in hydrated N_2 ; $T = 20^\circ\text{C}$.

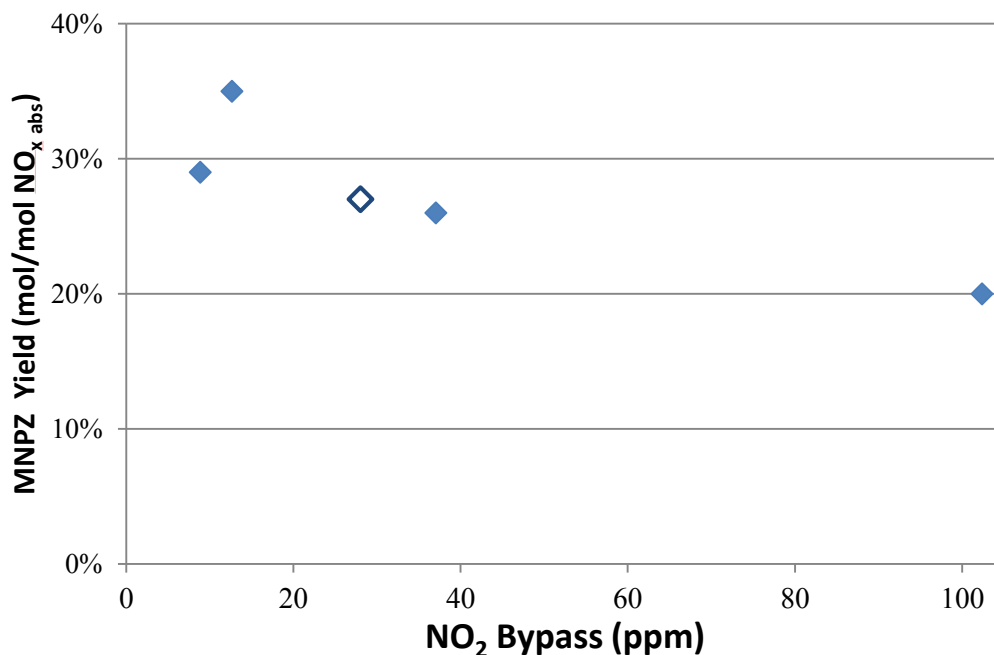


Figure 10: MNPZ yield in 1 m PZ with 100 ppm NO and varied NO₂ in hydrated N₂ (solid points) or air (open point); T = 20 °C.

3.5 NO_x Absorption into loaded 5 m PZ

A standard gas composition of 10 ppm NO₂ and 100 ppm NO in hydrated N₂ was sparged through loaded 5 m PZ to more closely simulate absorber conditions. MNPZ yield is independent of CO₂ loading and amine concentration as expected from the hypothesized termination mechanisms (Equations 14–16). Nitrosamine yield decreases drastically from 27% to 7% as temperature increases from 20 °C to 60 °C, possibly due to the decreased solubility of NO at higher temperatures (Figure 11). At 40 °C, nitrosamine yield is 17% which is roughly triple the nitrosamine yield found by Dai et al. at the same temperature. However, Dai et al. sparged with an NO₂:NO_x ratio of 1:2 [16], which favors termination as 2-PZOH instead of MNPZ.

One experiment was analyzed for 2-PZOH using the DNPH derivitization method. Although 2-PZOH concentrations were close to the quantification limit, it is clear that 2-PZOH increases with increasing absorbed NO_x (Figure 12). Since the stoichiometry of Equation 14 predicts 1 mol of 2-PZOH for every two moles of self-terminating amine radicals, the obtained yield of 65% is higher than expected. The high yield could possibly be explained by poor quantification of 2-PZOH at such low concentrations.

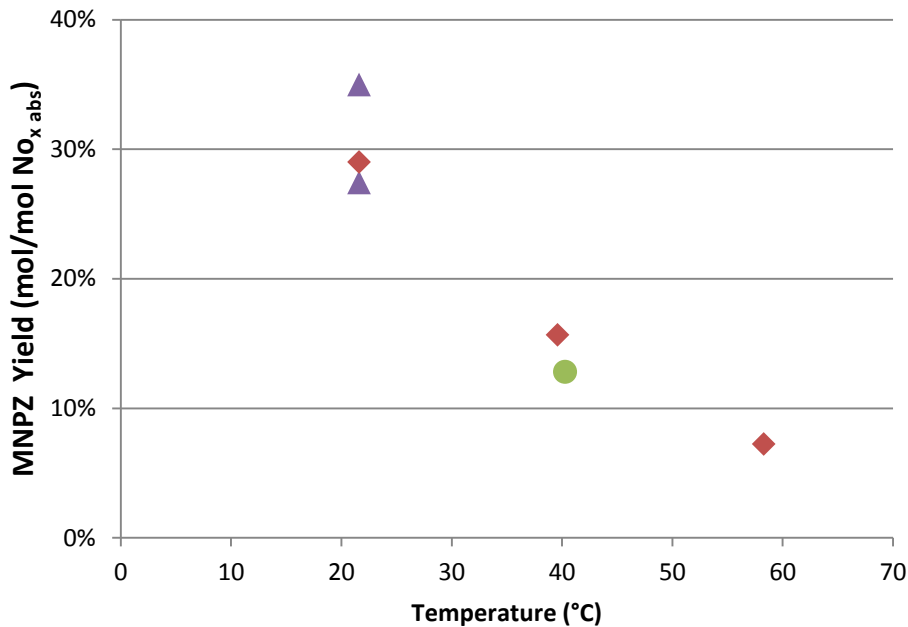


Figure 11: MNPZ yield in PZ with 10 ppm NO₂ and 100 ppm NO in hydrated N₂ for 5 m PZ α = 0.3 (red diamonds), 5 m PZ α = 0.15 (green circle) and 1 m PZ α = 0 (purple triangles).

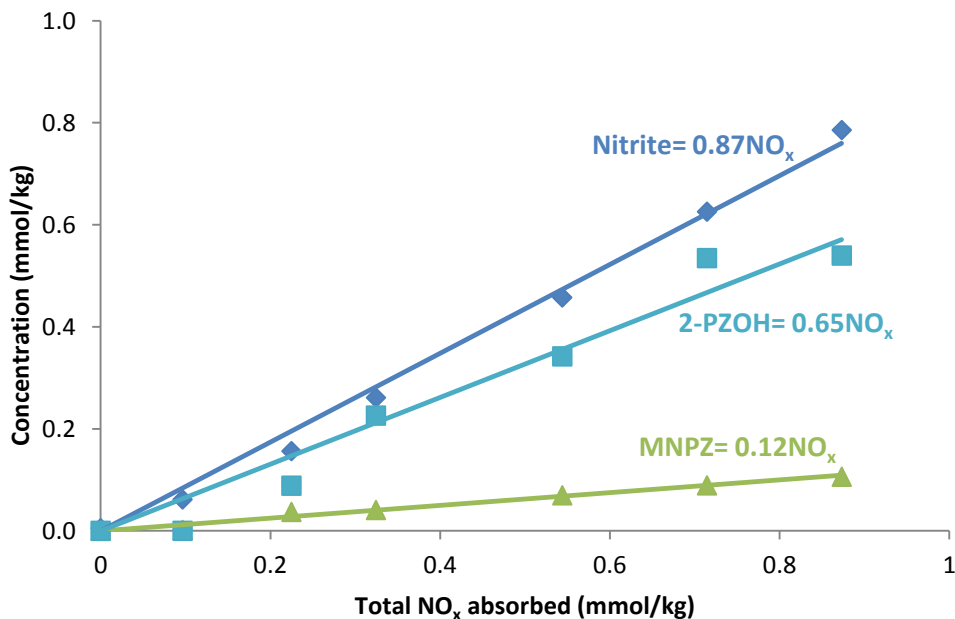


Figure 12: 2-PZOH accumulation from NO_x absorption in PZ; 10 ppm NO₂ and 100 ppm NO in hydrated N₂; 5 m PZ with α = 0.15 at 40 °C.

Two experiments were also performed with Inhibitor A (Inh A), a proprietary oxidative inhibitor that works as a free radical scavenger. As the concentration of Inh A increases, more of the PZ radical terminates by reacting with the scavenger instead of the NO. This decreases the MNPZ yield from 17% to 8% as Inh A increases from 0 to 200 mmol/kg (Figure 13). However, even though the MNPZ yield in the absorber decreases by 50%, this only has a minimum effect on the steady-state nitrosamine concentration since the absorbed nitrite will go on to nitrosate PZ under stripper conditions.

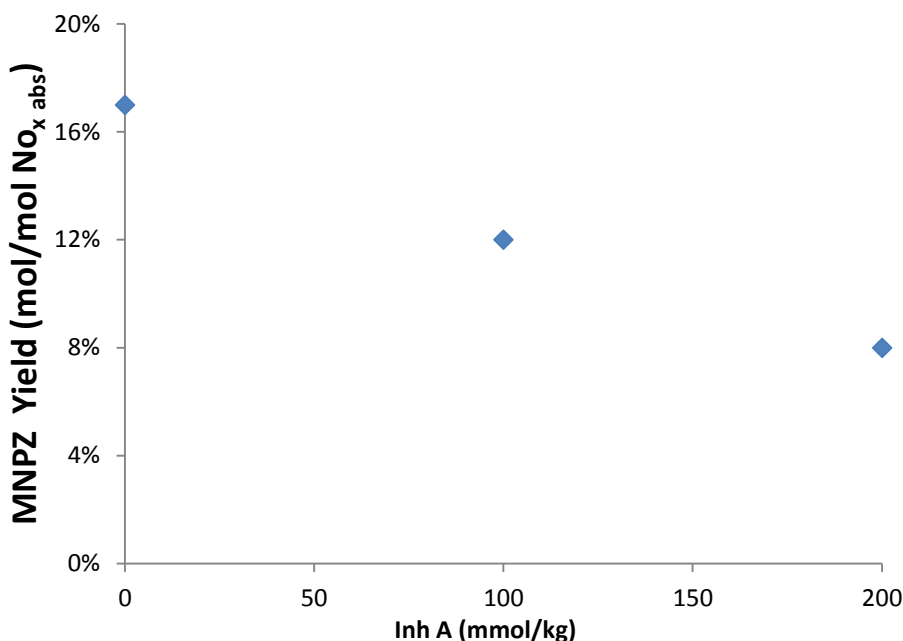


Figure 13: MNPZ yield with addition of Inh A; 10 ppm NO₂ and 100 ppm NO in hydrated N₂; 5 m PZ with $\alpha = 0.3$; T = 40 °C,

4. Conclusions

4.1 NO_x Absorption Kinetics

- NO_x absorption at ppm levels of NO_x is dominated by the free radical absorption of NO₂.
- Free radical absorption of NO₂ is first order in NO₂ partial pressure and half order in free amine concentration.
- Absorption can be modeled as mass transfer with fast reaction in the pseudo-first-order regime.
- NO₂ absorption kinetics are fastest with tertiary amines and slowest with primary amines similar to ClO₂ free radical absorption into amines.
- 70–99% of NO₂ will absorb in amine scrubbers designed to capture 90% of CO₂; only 4% of NO₂ absorption can be attributed to hydrolysis.
- A prescrubber with an A/G of $1 \cdot 10^6$ s·Pa·m²/mol can scrub 90% of flue gas NO₂ with 0.17 m free MDEA.
- MDEA oxidation is not catalyzed by NO₂ absorption in the presence of air and stainless steel metals.

4.2 NO_x Absorption Products

- 10 ppm of NO₂ absorbs into 0.1 m MDEA with a 95% nitrite yield and a 5% nitrate yield.
- Nitrite yield is independent of NO and oxygen, proving that the absorption species is NO₂ directly instead of N₂O₃.
- NO₂ hydrolysis through N₂O₄ becomes the dominating absorption mechanism when NO₂ partial pressure is above 10 Pa (100 ppm at atmospheric pressure).
- Nitrosamine is less than 3% of total absorption product in 0.1 m MDEA.
- NO can directly absorb into amine solution by reacting with the free radical formed by NO₂ absorption.
- In PZ solution, NO absorption forms MNPZ with yields of 20–35% of total absorbed NO_x at 20 °C.
- PZ free radicals can also react with themselves or free radical scavengers to lower the yield to MNPZ.
- MNPZ yield is independent of amine concentration and loading, but yield increases as the ratio of NO₂:NO_x decreases.
- PZ free radicals can also react with themselves or with free radical scavengers to lower the MNPZ yield.
- Increasing absorption temperature from 20 °C to 60 °C decreases MNPZ yield by 60% due to the decreased solubility of NO.
- MNPZ yield at 40 °C in 5 m PZ with an NO₂:NO_x ratio of 1:10 is 17% with nitrite closing the mole balance.
- High temperature nitrosation from nitrite is the dominating mechanism for nitrosamine formation in amine scrubbing.

Acknowledgements

This work was supported by the Texas Carbon Management Program at the University of Texas at Austin.

The authors declare the following competing financial interest(s): One author of this publication consults for Southern Company and for Neumann Systems Group on the development of amine scrubbing technology. The terms of this arrangement have been reviewed and approved by the University of Texas at Austin in accordance with its policy on objectivity in research. The authors have financial interests in intellectual property owned by the University of Texas that includes ideas reported in this paper

This article was developed under STAR Fellowship Assistance Agreement No. FP917625-01-0 awarded by the U.S. Environmental Protection Agency (EPA). It has not been formally reviewed by EPA. The views expressed in this article are solely those of Nathan Fine and EPA does not endorse any products or commercial services mentioned in this article.

Appendix A. Table of uncommon abbreviations and symbols

Abbreviation	Description	Unit
NO _x	Nitrogen oxides	-
NO	Nitrogen monoxide	-
NO ₂	Nitrogen dioxide	-
A	Fraction of NO _x absorbed in prescrubber	mol NO _x abs/mol NO _x flue
β	Fraction of NO ₂ absorbed as nitrite	mol NO ₂ abs/mol NO ₂ flue
γ	Fraction of NO absorbed as nitrosamine	mol NO abs/mol NO flue

δ	Yield of nitrosamine from nitrite	mol NNO/mol nitrite
MEA	Monoethanolamine	-
k_{str}	Pseudo-first order decomposition of nitrosamine	s^{-1}
τ_{str}	Residence time of the stripper	s
$\frac{G}{L}$	Ratio of molar flow rate of flue gas to volumetric flow rate of solvent.	mol flue gas/ L solvent
k_{ox}	Apparent rate of oxidation to nitrite	M/s
τ_{Tot}	Residence time of total scrubber	s
<i>NNO Steady State</i>	Steady state concentration of nitrosamine	M
NNO	Generic nitrosamine	-
$Am \cdot$	Amine radical formed from NO_2 absorption	-
N_2O_3	Dinitrogen trioxide	-
N_2O_4	Dinitrogen tetraoxide	-
WWC	Wetted wall column	-
N_{NO_2}	Molar flux of NO_2	mol/s m^2
K_g	Overall mass transfer coefficient of NO_2	mol/s m^2 Pa
$P_{NO_2 LM}$	Log mean average of the partial pressures of NO_2 into and out of the WWC	Pa
G_{WWC}	Gas flow rate across the WWC	mol/s Pa
A_{WWC}	Wetted area of the wetted wall column	m^2
k_g	Gas side mass transfer coefficient	mol/s m^2 Pa
k_g'	Overall liquid side mass transfer coefficient	mol/s m^2 Pa
HGF	High Gas Flow apparatus	-
$[NO_{2Abs.}]$	Total NO_2 absorbed into solution	mmol/kg solution
G_{HGF}	Gas flow rate across the WWC	L/min
m_{Sol}	Mass of absorbing solution	kg
$y_{NO_2 in}$	Mole fraction of NO_2 into the HGF	mol NO_2 /mol gas
$y_{NO_2 out}$	Mole fraction of NO_2 out of the HGF	mol NO_2 /mol gas
t	Total time sparged	min
MNPZ	N-nitrosopiperazine	-
2-PZOH	2-piperazinol	-
DNPH	Dinitrophenylhydrazine	-
k_{Am}	Rate constant for NO_2 reaction with amine	$M^{-1}s^{-1}$
D_{NO_2}	Diffusivity of NO_2 in amine solution	cm^2/s
H_{NO_2}	Henry's constant for NO_2 in amine solution	Pa m^3/mol
MDEA	Methyldiethanolamine	-
PZ	Piperazine	-
N_{OG}	Overall number of transfer units	-
A/G	Wetted area per gas flow rate	$m^2 s Pa/mol$
MAE	Methylaminoethanol	mol/kg H_2O
PZNO ₂	1-Nitropiperazine	-

References

- [1] Strazisar BR, Anderson RR, White CM. Degradation Pathways for Monoethanolamine in a CO₂ Capture Facility. *Energy & Fuels* 2003;17:1034–9.
- [2] Rochelle GT, Bishnoi S, Chi S, Dang H, Santos J. Research Needs for CO₂ Capture from Flue Gas by Aqueous Absorption/Stripping. Austin, Texas; 2001 Report No.: DE-AF26-99FT01029.
- [3] Shen C. Nitrogen Dioxide Absorption in Aqueous Sodium Sulfite [PhD Thesis]. Austin, Texas: The University of Texas at Austin; 1997.
- [4] Mimura T, Shimajo S, Mitsuoka S. Process for Removing Carbon Dioxide and Nitrogen Oxides from Combustion Gases. 5648053, 1997.
- [5] Takeuchi H, Ando M, Kizawa N. Absorption of Nitrogen Oxides in Aqueous Sodium Sulfite and Bisulfite Solutions. *Ind Eng Chem Process Des Dev* 1977;16:303–8.
- [6] Nedospasov AA. Is N₂O₃ the main nitrosating intermediate in aerated nitric oxide (NO) solutions in vivo? If so, where, when, and which one? *J Biochem Mol Toxicol* 2002;16:109–20.
- [7] Challis BC, Kyrtopoulos SA. Nitrosation under alkaline conditions. *J Chem Soc Chem Commun* 1976;21:877–8.
- [8] Sexton AJ. Amine Oxidation in CO₂ Capture Processes [PhD Thesis]. Austin, Texas: The University of Texas at Austin; 2008.
- [9] Voice AK. Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing [PhD Thesis]. Austin, Texas: The University of Texas at Austin; 2013.
- [10] Fine NA, Goldman MJ, Rochelle GT. Nitrosamine Formation in Amine Scrubbing at Desorber Temperature. *Environ Sci Technol* 2014;48:8777–83.
- [11] Goldman MJ, Fine NA, Rochelle GT. Kinetics of N-nitrosopiperazine formation from nitrite and piperazine in CO₂ capture. *Environ Sci Technol* 2013;47:3528–34.
- [12] Fine NA, Rochelle GT. Thermal decomposition of n-nitrosopiperazine. *Energy Proc* 2013;37:1678–86.
- [13] Fine NA, Nielsen PT, Rochelle GT. Decomposition of nitrosamines in CO₂ capture by aqueous piperazine or monoethanolamine. *Environ Sci Technol* 2014;48:5996–6002.
- [14] Pradhan MP, Joshi JB. Absorption of NO_x gases in plate column: Selective manufacture of sodium nitrite. *Chem Eng Sci* 2000;55:1269–82.
- [15] Patwardhan JA., Joshi JB. Unified model for NO_x absorption in aqueous alkaline and dilute acidic solutions. *AIChE J* 2003;49:2728–48.
- [16] Dai N, Mitch WA. Influence of Amine Structural Characteristics on N-Nitrosamine Formation Potential Relevant to Postcombustion CO₂ Capture Systems. *Environ Sci Technol* 2013;47:13175–83.
- [17] Chandan PA, Remias JE, Neathery JK, Liu K. Morpholine nitrosation to better understand potential solvent based CO₂ capture process reactions. *Environ Sci Technol* 2013;47:5481–7.
- [18] Jackson P, Attalla M. N-Nitrosopiperazines form at high pH in post-combustion capture solutions containing piperazine: a low-energy collisional behaviour study. *Rapid Commun Mass* 2010;24:3567–77.
- [19] Douglass M, Kabacoff B. The chemistry of nitrosamine formation, inhibition and destruction. *J Soc Cosmet Chem* 1978;606:581–606.
- [20] Dugas R. Carbon dioxide absorption, desorption, and diffusion in aqueous piperazine and monoethanolamine. The University of Texas at Austin, 2009.
- [21] Namjoshi O, Rochelle GT. Thermal degradation of PZ-promoted tertiary amine blends for CO₂ capture: comparison of structure effects and process conditions on degradation rate. *Int J Greenh Gas Control* *Manuscript Submitted*.
- [22] Nielsen PT, Li L, Rochelle GT. Piperazine degradation in pilot plants. *Energy Proc* 2013;37:1912–23.
- [23] Pacheco MA. Mass Transfer, Kinetics and Rate-based Modeling of Reactive Absorption. The University of Texas at Austin, 1998.
- [24] Bishnoi S. Carbon Dioxide Absorption and Solution Equilibrium in Piperazine Activated Methyldiethanolamine [PhD Thesis]. Austin, Texas: The University of Texas at Austin; 2000.
- [25] Dai N, Mitch WA. Effects of Flue Gas Compositions on Nitrosamine and Nitramine Formation in Postcombustion CO₂ Capture Systems. *Environ Sci Technol* 2014;48:7519–26.

- [26] Dai N, Shah AD, Hu L, Plewa MJ, Mckague B, Mitch WA. Measurement of Nitrosamine and Nitramine Formation from NO_x Reactions with Amines during Amine-Based Carbon Dioxide Capture for Postcombustion Carbon Sequestration. *Environ Sci Technol* 2012;46:9793–801.