Possible Ways to Minimize Nitrosation Reactions during Post-combustion CO₂ Capture Process

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Abstract

The formation and any emission of nitrosamines in a post-combustion CO₂ capture process are of great interest over the past few years even though its concentration is quite low. In the present research, bench scale nitrosation experiments were conducted using morpholine, a representative of secondary amines, with NO₂ gas and flue gas. Laboratory experiments with 5 M morpholine with 100 ppm NO₂ gas resulted in 88 µg/g nitrosomorpholine (NSMO) in 6 h and 450 µg/g in 24 h. However, coal derived flue gas gave only about 7 µg/g NSMO in 24 h. To prove the inhibitory effect from SO₂ in the flue gas, experiments were conducted with diluted NO₂ gas blended with SO₂ gas in the feed stream. Formation of NSMO was inhibited by about 53.3% when equal concentrations of SO₂ and NO₂ existed compared with the same concentration of NO₂ gas diluted with N₂. The inhibitory effect of SO₂ gas was found to be linear with its concentration. Apart from that, the addition of various inhibitors to the amine solution was also evaluated and isoascorbic acid was found as the best with 86% inhibition activity under the test conditions. Isoascorbic acid was further examined both under simulated CO₂ scrubber and stripper conditions indicating good stability and inhibition performance.

Graphical Abstract

Keywords

Amine degradation, CO_2 capture, flue gas, inhibitors, nitrosation, nitrosamines

1. Introduction

Though amine-based CO₂ capture processes are widespread in the petrochemical and natural gas cleanup industries, they are not without challenges for deployment into electric utility industry which needs to be addressed. For example, in addition to CO₂, a post-combustion flue gas stream carries various other impurities including trace metals, NO_x, SO_x, and halides which accumulates in the solvent as heat stable salts or react with the amine solvent causing irreversible solvent degradation (Chandan et al., 2013 b; Reynolds et al., 2012; Strazisar et al., 2003). Among these, nitrosation of amines is one of the concerned reactions due to its potential impact on human health.

Nitrosamines were identified in the 1950's as carcinogens in experimental animals. Since then, the existence of these compounds has been identified in numerous commercial products and industry processes, such as meats (IARC monograph, 2000), beer, cosmetics (IARC monograph, 2000; Flower et al., 2006; Schothorst and Somers, 2005; Schothorst and Stephany, 2001), rubber vulcanization, metal working fluids (IARC monograph, 2000; Ducos and Gaudin, 2003; Monarca et al. 1993), chlorinated and chloraminated water (IARC monograph, 2000; Wang et al., 2011; Pozzi et al., 2011), leather, tobacco products (IARC monograph, 2000), rocket fuel emissions, and the disinfection of water. The presence of these compounds has led to regulations around the globe to mitigate consumer or worker exposure.

Nitrosamine formation is an insignificant contributor to solvent loss in the CO₂ capture process (Dai et al., 2012; Fostas et al., 2011). Though stable nitrosamines are not formed directly from primary amines, such as monoethanolamine (MEA), primary amines can potentially contain impurities or degrade to components such as secondary amines. Secondary amines can form a

stable nitrosamine directly (Bedell et al., 2011; Fostas et al., 2011). Nitrosamines could be formed either in the vapor phase from amine atmospheric emissions or in the capture process solution (Nielsen et al., 2011).

There are several reports at present detailing nitrosation at post-combustion conditions in the lab and pilot scale. Dai *et al.* (2012) have reported 0.73 μM total nitrosamines for MEA and 59 μM for AMP/PZ system in the wash water at Statoil pilot plant. Nitrosamines have been detected in post-combustion CO_2 capture plant for soda ash production equipped with a deep-polishing SO_2 scrubber at Trona, California (Strazisar et al., 2003). About 5-47 ng/Nm^3 have been reported for the emission campaign at Maasvlakte (da Silva et al., 2013). A number of pathways and mechanisms have been proposed for the formation of nitrosamines from nitrate, nitrite, and amines in neutral and acidic conditions (Lv et al., 2008; Masuda et al., 2000; Sun et al. 2010). Recently, our group and others have reported the nitrosamine formation pathway and kinetics from NO_2 and nitrite under post-combustion solvent compositions (Chandan et al., 2013a; Goldman et al., 2013).

Regarding the fate of nitrosamine after formation, several pathways have been identified. They decompose rapidly by exposure to UV light to form aldehydes, nitrogen, and nitrous oxide or amine and nitrous acid (Shah et al., 2013; Dai and Mitch, 2013). However, the UV method is applicable to the water wash solution only. Some literature reported rapid denitrosation under acidic conditions in the presence of nucleophiles such as iodide, thiocyanate, bromide or chloride (Ikeda and Migliorese, 1990). They are also decomposed by prolonged thermal treatment (Chandan et al., 2013a; Fine and Rochelle, 2013; Fine *et al.*, 2014). However, thermal decomposition is difficult to be feasible at predefined stripper operating conditions for each amine.

Here, ways to *in-situ* minimize nitrosamine formation are presented in the context of post-combustion CO₂ capture conditions. Morpholine was chosen as the representative of the group of secondary amines since nitrosomorpholine (NSMO) is easily available as a standard for GC-MS quantification. Experiments were conducted on CAER post-combustion pilot-plant with coal derived flue gas and a notable inhibitory effect was observed when compared with the laboratory experiments with NO₂ gas. To verify the role of SO₂ from flue gas in the nitrosamine formation, experiments were conducted by blending SO₂ gas with NO₂ gas in the feed stream with different concentrations. In addition, a series of commercially available and cost effective additives were tested in 5M morpholine solutions to study their impact on nitrosamine formation. A few recent studies have discussed the use of oxidative inhibitors during CO₂ capture processes (Goff and Rochelle, 2006; Supap et al, 2011) but have not evaluated for nitrosation. The activity of the inhibitor was compared to that of the baseline under conditions consistent with CO₂ capture scrubber and stripper conditions. The focus of this study is to develop of a viable approach towards eliminating nitrosamine formation *in-situ* during a CO₂ capture process.

2. Experimental

2.1. Chemicals

500 ppm SO₂ in N₂ and 100 ppm NO₂ in N₂ gas cylinders (>99.9% purity) were purchased from Scott Gross. Morpholine, sodium nitrite, ascorbic acid, glucose, and vitamin E were purchased from Acros Organics. Isoascorbic acid and nitrosomorpholine (NSMO) were purchased from Sigma-Aldrich. Vanillin was purchased from TGI Chemicals and ethoxyquin was obtained from MP Biomedicals.

2.2. *Reaction procedure*

The reactions were conducted in a 100 mL 4-necked round bottom flask fitted with a condenser at the gas outlet. The apparatus was immersed in an oil bath to control the reaction temperature (± 2 °C) with a calibrated K-type thermocouple immersed in the solution. For a typical reaction, 100 mL of 5 M amine solution in DI water was taken into the flask. 100 ppm NO₂ in N₂ gas from the cylinder (or flue gas) was passed into the reaction medium with a desired flow rate controlled by a flow meter (0 - 2.36 L/min, McMaster Carr). For reactions with SO₂, 500 ppm SO₂ gas was passed through the flow meter at a desired rate (0 - 0.185 L/min, McMaster Carr) and mixed with 100 ppm NO₂ gas before reacting with the solution. The outlet gas from the flask was bubbled into a 2.5M KOH bath to trap any excess NO₂ and nitrosamines before venting into the fume hood. The experiment was conducted for at least 6 h at the selected temperature. The samples were collected and analyzed by the methods described below.

For high temperature (e.g. stripper conditions) studies, the experiments were conducted in a sealed container to study the nitrosamine formation/destruction using a nitrosating agent, sodium nitrite, to determine the functionality of a selected additive under severe conditions. 5 mL of solution containing an amine and 1000 ppm sodium nitrite was added to the cylinders (reactors) constructed with ½ inch OD 316 stainless steel tubing (10 mL volume) and sealed at both ends. Reactors were kept at 125, 135, and 145 °C and at autogenous pressure using temperature controlled ovens. Reactors were taken out of the ovens at 5, 10, 15, 20 and 25 h. The weights of the reactors were recorded before and after heating to measure the weight loss if any for leak checking and quality control purposes. The samples were collected and analyzed.

2.3. *Analysis of samples*

The products of morpholine experiments were analyzed on a GC-MS Saturn 2200 Varian instrument equipped with a single quad mass analyzer and a DB-5 capillary column (0.25mm i.d.×30m) using 1 ml/min helium flow rate. MS was used to scan in the range of 50-500 amu. Peak identification was carried out in SIM (selective ion mode). Samples were prepared for GC-MS analysis using an extraction method reported previously (Chandan et al., 2013a). Quantification of the nitrosomorpholine (NSMO) was based on the calibration plot from standard samples prepared in dichloromethane. The amount of NSMO obtained from GC-MS was divided by the respective sample weight to get the actual value in µg/g.

Anion Ion Chromatography (IC) was utilized to identify and quantify sulfate and nitrite ions. A Dionex ICS-3000 ion chromatograph system (AS40 autosampler, ICS 3000 DP-1 dual pump, ICS 3000 EG-2 eluent generator and an ICS 3000 conductivity detector) was used. For IC analysis, 50 µL of sample was taken and diluted with 4.95 mL of deionized water. Peaks were quantified from a standard calibration curve based on a known analytical standard. Each sample was run twice for quality control measures. A blank solution was run before and after each set of analysis.

3. Results and Discussion

3.1. Nitrosamine measurement with NO₂, NO_x and coal-derived flue gas

Field-testing carried out at CAER with coal derived flue gas has indicated inhibitory effect of flue gas components on the nitrosation reaction. A slipstream of the coal-derived flue gas is treated with pollution control devices, including particulate separation and flue gas desulfurization, before being used in the experiment. The typical flue gas compositions from the CAER coal-combustor after flue gas desulfurization (FGD) are 10-12% CO₂, 200ppm NO_x, 50-

100ppm SO₂, and others. It is our understanding that the presence of only NO is unlikely to form nitrosamine formation unless O₂ is present which converts NO via NO₂ to either N₂O₃ or N₂O₄. (Challis et al., 1978; Challis and Kyrtopolous, 1979).

Laboratory tests with cylindered 100 ppm NO₂ gas for 5 M morpholine solution resulted in 88 µg/g of nitrosamine in 6 h. The nitrite obtained in that case was 208 ppm (Table 1, Entry 1). The resulted high amount of nitrite was due to the faster hydrolysis of NO₂, N₂O₃ and N₂O₄ in the reaction medium. Nitrite is also counter product of nitrosation reaction through N₂O₃. Bubbling 100 ppm NO₂ for 24 h resulted in 450 µg/g NSMO and 1265 ppm nitrite (Table 1, Entry 2). The role of NO₂ for nitrosamine formation was also studied by using a gas primarily composed of NO (500 ppm NO_x) for 6 h at 30 °C, under these conditions the NSMO formation was 22 µg/g and nitrite was 35 ppm (Table 1, Entry 3).

The reactions of morpholine with coal-derived flue gas were conducted for 6 and 24 h at 30 °C with same gas flow rate as laboratory experiment. There was no formation of NSMO in 6 h and no nitrite was observed (Table 1, Entry 4). For the 24 h run, the amount of NSMO obtained was only 7 µg/g and nitrite was 12 ppm (Table 1, Entry 5). One of the reason behind the lower NSMO concentrations in 24 h is most of the flue gas containing NO_x gas was NO and as shown in Entry 3, only NO was less likely to be responsible for nitrosation. Another reason behind the low concentrations could be the presence of other flue gas components such as SO₂, or heat stable salts. Therefore, it was valuable to study their effects on nitrosamine formation.

3.2. *Effect of SO₂ gas*

The main constituent of NO_x and SO_x content in the coal-derived flue gas are NO and SO₂ respectively. The presence of SO_x significantly increases the number of possible reactions due to

interaction between nitrogen and sulfur species. During transportation of flue gas, formation of both sulfuric and nitric acid has been observed in the literatures. Two main reaction paths have been proposed for its formation. The first reaction path is the homogenous gas phase oxidation of SO₂ by NO₂ (equation 1). The SO₃ formed will be absorbed in water and react to sulfuric acid (equation 2). The second possible reaction path is based on the formation of H₂SO₃ and HNO₂ as a result of absorption of SO₂ and NO_x in water. Subsequently, HNO₂ oxidizes H₂SO₃, which results in the formation of sulphuric acid and N₂O (equation 3) (Ajdari et al., 2013). It has also been reported that the active species in the nitrosation reaction, N₂O₃, reacts with SO₂ (equation 4) (Shen and Rochelle, 1998) to make sulfuric acid. Thus in both the cases, there is conversion of nitrosating agent and thus nitrosamine formation could be possibly inhibited.

Under the experimental conditions studied here, SO₂ and substances which can co-exist, such as sulphites, bisulphites, metabisulphites and thiosulphates, reduce nitrites and active forms of NO_x to the forms which do not cause nitrosations. (Douglas et al., 1978; Gray and Dugan, 1975). Therefore, in order to verify whether the presence of SO₂ could impact the formation of nitrosamines, a series of well-controlled experiments were conducted with results reported below.

During these experiments, 500 ppm SO₂ (balance nitrogen) was blended with 100 ppm NO₂

gas (balance nitrogen) as the feed stream. Reactions were conducted with 5 different flow rates: (0-189 mL/min) for SO_2 + 0.95 L/min for NO_2 . The actual concentrations of NO_2 and SO_2 gases in the mixture were calculated and listed in Table 2. Due to experimental design limits, the NO_2 concentration in the feed gas stream also decreased. However, the magnitude of NSMO reduction was larger than the dilution of NO_2 gas. To prove the inhibiting role of SO_2 , another set of experiments was conducted with nitrogen instead of SO_2 gas so the concentration of NO_2 gas remained the same. Here, the amount of NSMO obtained was more than the SO_2 containing experiments at all concentrations (Table 2). Entry 1 is a baseline study without the addition of SO_2 gas, and 88 $\mu\text{g/g}$ of NSMO was observed. As the concentration of SO_2 gas was increased from 11 to 84 ppm, the NSMO amount dropped from 73.2 to 30.9 $\mu\text{g/g}$ (Entry 2 to 5). Under the same testing matrix, the use of nitrogen instead of SO_2 dropped the NSMO concentration from 82.8 to 66.1 $\mu\text{g/g}$. When NO_2 and SO_2 concentrations were equal (Entry 5), NSMO was 53.3% inhibited as compared with the similar NO_2 concentration obtained by diluting with N_2 as shown in Entry 5.

For simulating the amine scrubbing solution in the post combustion CO_2 capture process, one model experiment was conducted with CO_2 loaded morpholine solution ($\text{C/N}=0.4$). This solution also showed 52.7% inhibition when 84 ppm NO_2 and 84 ppm SO_2 were present as compared with 84 ppm NO_2 only (Entry 6). Thus, it is reasonable to conclude that the presence of SO_2 inhibits the nitrosation reaction. Under real operating conditions with coal-derived flue gas, the amount of SO_2 will be higher than the amount of NO_2 thus nitrosamine formation is believed to be greatly affected. Under coal-derived flue gas environment, the reaction of NO with SO_2 under aqueous condition will also lead to the formation of sulfate as shown below in equation 5. However, in the presence of SO_3 , a component of SO_x , NO is oxidized to generate SO_2 and NO_2

(equation 6) and thus may facilitate nitrosation reaction to some extent.

In overall, the total amount of NSMO after 6 h decreased linearly with increasing SO_2 concentration in the feed gas streams (Figure 1). Sulfate concentration in the solution was increased with higher SO_2 loaded runs indicating the conversion of SO_2 to sulfate during the course of reaction. Sulfate is not expected to be an inhibitor for the process and has been confirmed with a separate nitrosation experiment with external sulfate addition. The pH change for all the experiments was almost similar. In reality it is a common practice that amine based CO_2 scrubbing employ a polishing scrubber to lower SO_x concentration to less than 10 ppm for reducing amine degradation and heat stable salt (HSS) formation. As observed, at low SO_2 concentration, the inhibition was very limited; an alternative solution would be to add inhibitors to reduce the nitrosamine formation in the process.

3.3. Evaluation of inhibitors

Inhibitors have been known for reducing the impact of radical reactions in aqueous environments. A number of nitrosation inhibitors under various reaction conditions, specifically acidic conditions, have been reported previously (Douglass et al., 1978). However, inhibition impact on nitrosation in highly concentrated amines system for a CO_2 capture from a utility power plant has remained unexplored.

Here, six inhibitors including glucose, vanillin, α -tocopherol, ascorbic acid, isoascorbic acid, and ethoxyquin with 5 mM concentration were screened for the first time for their inhibition

activity towards nitrosamine formation in 5 M morpholine solution under utility operating conditions. These inhibitors have been previously studied under acidic conditions with one or the other amine towards their nitrosation activity (Bartsch et al., 1993; Bharucha et al., 1985; Bharucha et al., 1987; Perez et al., 1990; Tannenbaum et al., 1991). In the field of biologic and biomedical studies, nitrosation of morpholine in the presence of ascorbic acid has been reported by Perez et al. during mutagenic activity in mice under low pH conditions (Perez et al., 1990). Ethoxyquin has been studied as an anti-nitrosamine agent for bacon. The mode of action for ethoxyquin has been reported in a few publications (Bharucha et al., 1985; Bharucha, 1987). These additives except ethoxyquin were also selected based on their higher solubility in aqueous amine solutions. However, the impact of other flue gas components such as oxygen was not considered here and the activity was tested purely for nitrosation.

From Figure 2, it was observed that the inhibitors generally seem to retain their activity for the full course of the experiment. The activity of all screened inhibitors was sacrificial meaning it changed its chemical structure while scavenging free radicals (Brannegan, 2010; Leis and Rios, 1995). The results of inhibition activity are summarized in Table 3. A baseline experiment without any additive is represented in Entry 1. Glucose did not show any inhibition activity (Entry 2) whereas 95% inhibition was achieved with ethoxyquin (Entry 7). Though ethoxyquin showed the highest inhibition activity, it was mostly insoluble in the concentrated amine solution tested here, which could cause problems in a CO₂ capture process where the un-dissolved inhibitor may, for example, get trapped in filters or deposited on the packing surface. The impact of α -tocopherol (Entry 3) and vanillin (Entry 4) was smaller which might be due to the phenolic nature of these compounds. Ascorbic and isoascorbic acid gave 83% and 86% inhibition respectively (Entry 5 and 6). For amine scrubbing systems it would be valuable to determine the

activity of the inhibitors simultaneously with the main CO₂ capture reaction, thus a representative reaction with CO₂ loaded morpholine solution was conducted using 5 mM isoascorbic acid as an inhibitor and 82% inhibition was obtained (Entry 8). It might be possible that the presence of other flue gas impurities will affect the behavior of an additive; however such impacts were not studied for this paper.

The amount of nitrite formed during the course of the experiment (6 h) was plotted against % inhibition (Figure 3) for each reaction. The nitrite content was much higher for the samples with inhibitor than the baseline. The possible mechanism for higher nitrite formation is the reaction of the inhibitor with NO₂. A radical charge on NO₂ gas could acquire an electron from the additive to form a nitrite ion, thus the amount of nitrite is much higher with inhibitors.

Isoascorbic acid was further chosen as an inhibitor due to its high inhibition activity compared to others as shown in Table 3. Different amounts of isoascorbic acid were added at 30 °C to the solution (Figure 4). Based on the increasing slope of the 1 mM loading curve of nitrosamine concentration it is clear that isoascorbic acid is being consumed and 1mM was not sufficient to control the nitrosation reaction. At the 5 mM concentration the response remains linear indicating that the inhibitor is present in sufficient quantities to limit acceleration of NSMO formation under the experimental conditions. At 50 mM concentration, the amount of NSMO was below the detectable limits. Thus with greater amounts of isoascorbic acid, more substantial and longer inhibition was seen.

For isoascorbic acid 5 mM, the concentration of nitrite was 1150 ppm. It has been observed that nitrite does not react with morpholine at 30 °C to give NSMO but at higher temperatures nitrite was an active nitrosating agent (Chandan et al., 2013a). If the inhibitor loses its activity at

high temperature, then the nitrite generated at lower temperatures in the absorber could react with an amine under stripper conditions. The stability and activity of isoascorbic acid was thus studied at higher temperatures to prove its capability for a complete CO₂ capture cycle. Here experiments were conducted with 1000 ppm sodium nitrite and 25 mM isoascorbic acid in 5 M morpholine solution at 125, 135, and 145 °C for 25 h. Isoascorbic acid is known to decompose above 180 °C. The amount of NSMO formed was lower with inhibitor (Figure 5) at all three temperatures. At higher temperatures, nitrite gets converted to NO in the presence of inhibitor, thereby preventing nitrosation of the amine (Leis and Rios, 1995; Licht et al., 1988). Thus in the actual capture process, inhibitor is believed to retard both pathways, one is to prevent NO₂ gas reaction with amine and the other to prevent nitrite reaction with amine.

4. Conclusion

Nitrosation studies of morpholine solution with the CAER flue gas showed inhibitory impact compared with the laboratory tests which was due to the presence of SO₂ in the flue gas. NSMO concentration was inhibited by about 53.3% in the presence of equal concentrations of NO₂ and SO₂ gas in comparison with the same concentration of NO₂ diluted with N₂. Six inhibitors screened here were shown to be effective in reducing nitrosamines. Isoascorbic acid was found to give the most 86% inhibition of NSMO in 6 h, and it was efficient at both the high and low temperature nitrosation conditions for morpholine.

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444

Table 1. NSMO formation with NO₂ gas and CAER derived flue gas

#	Reaction conditions	Reaction time (h)	Nitrite amount from IC (ppm)	Amount of NSMO (µg/g)
1	100 ppm NO ₂	6	208	88
2	100 ppm NO ₂	24	1265	450
3	500 ppm NO _x	6	35	22
4	Flue gas	6	0	0
5	Flue gas	24	12	7

Reaction conditions: 100 mL 5M morpholine solution, 0.95 L/min gas flow rate, 30 °C

Table 2. NSMO for reactions with NO₂-SO₂ blends and NO₂ blended with additional N₂ with 5M morpholine at 30 °C for 6 h

#	Flow rate (L/min)			Gas conc. (ppm)		Sulfate conc. ^a (ppm)	NSMO conc. ^b (µg/g)		% inhibition considering dilution with N ₂
	NO ₂	SO ₂ /N ₂	Total	NO ₂	SO ₂		With SO ₂	With N ₂	
1	0.95	-	0.95	100	0	0	88.0	88.0	0
2	0.95	0.024	0.974	97	11	35	73.2	82.8	11.6
3	0.95	0.047	0.997	95	23	86	67.4	79.4	15.1
4	0.95	0.095	1.045	91	45	201	45.5	73.5	38.1
5	0.95	0.189	1.139	84	84	264	30.9	66.1	53.3
6*	0.95	0.189	1.139	84	84	269	31.6	66.8	52.7

^aAnalyzed by IC for SO₂ containing experiments

^bAnalyzed by GC-MS

*Experiment with CO₂ loaded 5M morpholine solution C/N = 0.4

Table 3. Inhibitor screening for nitrosation of 5M morpholine with 5mM inhibitor and 100 ppm NO₂ gas flow rate 0.95 L/min at 30 °C for 6 h

#	Inhibitor	Amount of NSMO (µg/g)	Inhibition activity (%)*
1	No Inhibitor	88	-
2	Glucose	88	0
3	α-Tocopherol	54	39
4	Vanillin	47	46
5	Ascorbic acid	14	83
6	Isoascorbic acid	12	86
7	Ethoxyquin	4.5	95
8	Isoascorbic acid**	16	82
*% inhibition = ([Nitrosamine] _{blank} - [Nitrosamine] _{inhibitor})/[Nitrosamine] _{inhibitor} × 100			
**Experiment with CO ₂ loaded 5M morpholine solution C/N = 0.4			

Figure 1

Figure 1. Linear relationship between increased SO₂ concentration and decreased NSMO amount

Figure 2

Figure 2. Effect of different inhibitors

Reaction conditions: 5M morpholine, 5mM inhibitor, 100 ppm NO₂ gas, flow rate 0.95 L/min, 30 °C, 6 h

Figure 3

Figure 3. Nitrite concentration at the end of reaction for each 5 mM additive and their % inhibition

Figure 4

Figure 4. Effect of inhibitor quantity

Reaction conditions: 5 M morpholine, isoascorbic acid, 100 ppm NO₂ gas, flow rate 0.95 L/min,
30 °C, 6 h

Figure 5

Figure 5. Inhibitor evaluation at higher temperature for morpholine nitrosation

Reaction conditions: 5 M morpholine, 1000 ppm sodium nitrite, 25 mM isoascorbic acid, 25 h