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FORMATION AND MEASUREMENT OF N_2O IN COMBUSTION SYSTEMS

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Direct N_2O emissions from fossil fuel combustion have previously been reported to be equivalent to 25–40% of the NO_x levels. At these levels, fossil fuels have been suggested to be a major anthropogenic source of N_2O. Recent tests have shown these measurements to be in error, most of the N_2O having been formed by reaction between NO_x, SO_2, and H_2O in the sample containers. Time resolved measurements of gas samples stored in Tedlar bags, supported by chemical kinetic calculations, indicate that the majority of N_2O forms over a time period of 6 hours. The conversion of NO_x to N_2O in the sample containers is shown to depend on the amount of SO_2 present.

This sampling artifact raises questions about the validity of the existing data base, collected by grab sampling methods. As a result, a continuous infrared analyzer, developed primarily for characterization of N_2O emissions from full scale combustion sources, was used to perform on line N_2O measurements at several full scale utility combustion systems. A variety of conventional and advanced utility combustion systems (firing pulverized coal, oil, and gas) were tested. The measurements from conventional systems (natural gas, oil, and pulverized coal-fired) indicate that the direct N_2O emission levels are generally less than 5 ppm and are not related to the NO_x levels in the flue gas. However circulating fluidized bed units produced elevated N_2O emissions. At one circulating fluidized bed combustor firing a bituminous coal, N_2O levels ranged from 84 to 126 ppm as the load was varied from 100% to 55%, respectively. The N_2O emissions from the circulating fluidized bed appeared to be inversely related to the bed temperature. However, temperature is not the only parameter affecting N_2O emissions from fluidized beds; all three of the units studied operated at similar temperatures during full load operation, but the N_2O emissions ranged between 25 and 84 ppm. N_2O emissions were also elevated at a full-scale boiler using selective non-catalytic NO_x reduction with urea; 11–13% of the reduced NO_x was converted to N_2O.

Background

The mean global concentration of N_2O is approximately 300 ppb and has been increasing at a rate of 0.2–0.4% per year.[1,2] In the troposphere, N_2O is a relatively strong absorber of infrared radiation, and, therefore implicated as a contributor to the "Greenhouse Effect." Being stable in the troposphere, N_2O is transported to the strato- sphere. In the stratosphere N_2O is the largest source of stratospheric NO; NO is the primary species responsible for establishing the equilibrium stratospheric O_3 concentration.[3]

The increase of N_2O in the atmosphere has been attributed to anthropogenic sources, although the dominant source of N_2O is still uncertain. Weiss,[2] Hao et al.,[4] and Tirpak[1] suggest that combustion of fossil fuels results in emissions of N_2O that can ac-

count for the observed increase in N_2O. Previous N_2O measurements from combustion sources indicate that systems fired with natural gas do not produce significant concentrations of N_2O. However, substantial levels of N_2O were reported from systems fired with residual oil or coals (e.g., fuels containing nitrogen and sulfur). In fact, the measurements of Hao et al.[4] and Castaldini et al.[5] suggest that the N_2O emissions are related to the emissions of NO_x (NO + NO_2); the N_2O level being equal to 25–40% of the NO_x concentration.

The N_2O measurements from combustion sources referenced above were made by gas chromatographic analysis of gas samples collected in glass or stainless steel containers. Recent measurements have shown that these grab samples can undergo chemical reaction in the containers creating N_2O concentrations substantially higher than those originally formed in the combustion process.[6,7] This raises questions regarding the existing data base on N_2O emissions from combustion sources and the role of combustion in contributing to the increases in atmospheric N_2O concentration.

This paper will address two issues: 1) the formation of N_2O in sample containers; and 2) N_2O emissions from combustion systems using an on-line continuous infrared analyzer.

Formation of N_2O in Sample Containers

The artifact in measuring N_2O with grab sampling techniques was initially identified in the course of combustion experiments in a bench-scale combustor.[6,7] The tests showed that the N_2O was being formed in the sample containers through a reaction mechanism involving SO_2, NO, and H_2O.[6,7] The SO_2 concentration was found to influence the amount of N_2O formed. To better quantify the progress of the reactions occurring in the sample containers, tests were conducted during this study to determine the time history of N_2O, NO, NO_2, and SO_2 in the sample containers. Gas samples from a natural gas fired combustor were collected in 270 liter Tedlar bags and subsequently analyzed for NO, NO_2, N_2O and SO_2. The 270 liter Tedlar bags provided sufficient sample to allow samples to be withdrawn and analyzed as a function of time using continuous gas analyzers. N_2O was analyzed with an infrared continuous analyzer described in Ref. 8. NO and NO_x were measured with a TECO chemiluminescent analyzer and SO_2 with a Western Research ultraviolet analyzer.

The primary variable for the series of tests was SO_2 concentration, which was varied from 700 ppm to 2500 ppm. Initial SO_2 and NO_x concentrations were varied by adding SO_2 to the combustion air and NH_3 to the natural gas. The time histories of N_2O, NO_x, and SO_2 are shown in Fig. 1. As can
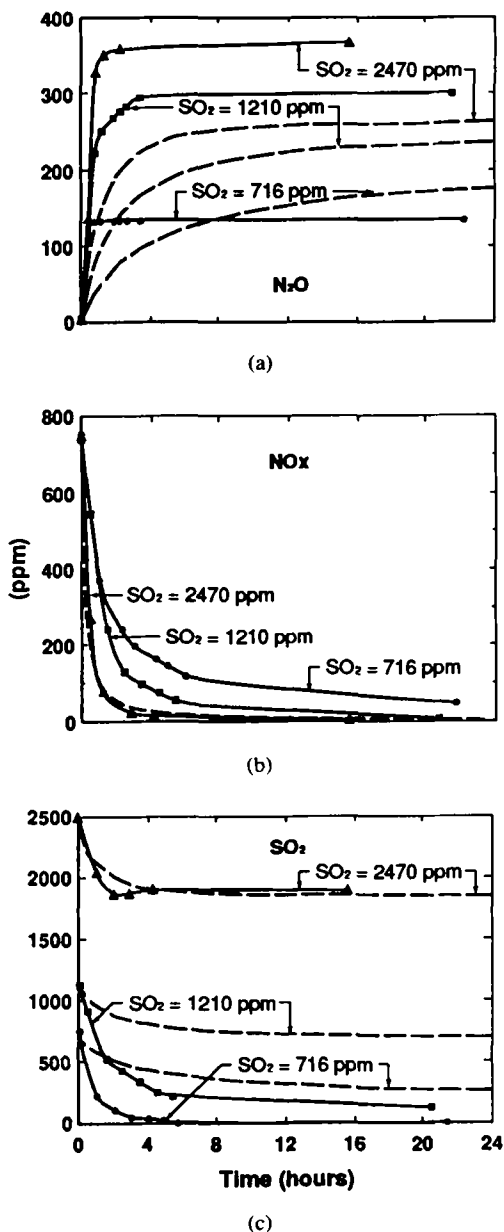

(a)

(b)

(c)

FIG. 1. Time histories of N_2O, NO_x, and SO_2 during reaction in 270 liter Tedlar bags: experimental versus model results: a. N_2O, b. NO_x, c. SO_2 (——— experimental, --- model).

be seen in Fig. 1a, the majority of the N_2O formation occurs in the first six hours, irrespective of the initial SO_2 level. The accompanying time histories of NO_x and SO_2 are shown in Figs. 1b and 1c. As seen in Figs. 1a–c, at the high SO_2 condition, virtually all of the NO_x initially present in the

Tedlar bag is transformed to N_2O in the final product. At the lowest SO_2 concentration (716 ppm), N_2O continues to form until virtually all of the SO_2 is removed from the gas phase, after which the N_2O stabilizes while the NO_x continues to decrease. At the intermediate SO_2 level (1210 ppm), the N_2O formation rate is initially rapid becoming more gradual after 2 hours, as the NO_x and SO_2 are consumed. For this intermediate case, there appears to be sufficient SO_2 to allow the reaction to proceed longer than at the low SO_2 condition, but not sufficient SO_2 to convert all of the initial NO_x to N_2O, as was observed at the higher SO_2 level.

The gas phase and aqueous reactions between SO_2, NO_x, and H_2O leading to the formation of N_2O have been documented in the literature. Martin et al.[9] discuss the reaction mechanism; the general chemistry has also been discussed in the wet FGD scrubbing literature.[10,11] Lyon and Cole[12] proposed a detailed mechanism for N_2O formation in the sample containers. In the sample flasks, NO is oxidized to NO_2. NO_2 and SO_2 in the gas phase are taken to be in equilibrium with the aqueous phase. In the aqueous phase, the NO_2 and SO_2 ultimately form N_2O and H_2SO_4 through a reaction sequence involving HNO.[12]

The detailed mechanism of Lyon and Cole was integrated for the same conditions as the experiments conducted in the Tedlar bags (Fig. 1). The results of these calculations are included with the experimental results in Figure 1a–c. In general, the model calculations are in qualitative agreement with the experimental results. The characteristic time for N_2O formation is basically the same between experiment and model, with the experiment exhibiting somewhat faster N_2O formation than predicted by the model. However, there are noteworthy differences between the experiments and the model calculations. First, for the medium and high SO_2 cases, the kinetics underpredict the amount of N_2O formed. At the high SO_2 condition, the experiments exhibited virtually 100% conversion of the NO_x to N_2O, whereas the model predicts 65% conversion. Second, in the Tedlar bags the rate of disappearance of NO_x decreased as the SO_2 level decreased, whereas the kinetic calculations indicate little effect of SO_2 level upon the NO_x time histories. Another difference between the experimental observations and calculations is the effect of the chemical reactions on the pH of the aqueous phase. Experimentally, the pH in sample containers containing 600 ppm NO and 1500 ppm of SO_2 have been reported to be 1.8.[7] However, the calculations indicate an aqueous phase pH of only 4.5–4.8 after 24 hours for initial SO_2 concentrations ranging from 2470 ppm to 100 ppm. This is expected to influence the calculated levels of N_2O produced since previous work suggests that N_2O increases as the pH decreases.[10,11]

At present, the model does not include a reaction allowing the direct oxidation of sulfite ion to sulfate ion, although this step is known to occur. By including this reaction in the model, most of the deviations noted in Fig. 1 could be accounted for. For example, the sulfite ion concentration would be depleted, reducing the resistance of the liquid phase to SO_2 dissolution. This would increase the predicted rate of SO_2 decay in the gas phase, improving agreement between model and experiment (Fig. 1). Also, the depleted sulfite ion in the liquid phase would slow the liquid phase conversion of nitrogen, thereby increasing the resistance of NO_2 entering the liquid phase. Finally, the missing reaction would accelerate the conversion of a weak acid into a strong acid, reducing the predicted pH toward the experimentally observed values of 1.7–1.9.

N₂O Emissions from Combustion Sources

Reliable measurements of N_2O emissions from combustion systems are needed in order to assess the role of combustion as an anthropogenic source of atmospheric N_2O. With grab sampling procedures in question, a continuous N_2O analyzer, utilizing a non-dispersive infrared principle was used to characterize N_2O emissions from a variety of utility scale combustion systems. The continuous N_2O analyzer system is described in detail elsewhere.[8] The basic analyzer is a non-dispersive infrared analyzer manufactured by Horiba Ltd. based on the work by Montgomery, et al.[8] The analyzer utilizes a 500 mm sample cell and uses the 7.8–8.5 micron region of the infrared for the N_2O measurement. To eliminate interferences, NO_2 and SO_2 are removed from the sample gas using 1 M solutions of sodium sulfite and sodium carbonate.[8]

The continuous N_2O analyzer was used to characterize the N_2O emissions from the following systems:

Natural Gas-Fired Utility Boilers	(3 units)
Residual Oil-Fired Utility Boilers	(2 units)
Pulverized Coal-Fired Utility Boilers	(7 units)
Circulating Fluidized Bed Combustors	(3 units)
Boiler with Selective Non-Catalytic	
NO_x Reduction	(1 unit)

The units firing natural gas, oil, and pulverized coal comprised a variety of designs including single wall-fired, opposed wall-fired and tangentially fired, and ranged in size from 50 to 750 MW (electric). The majority of the testing was performed at full load. For selected sites, the testing was performed over a range of loads. A summary of the results is pre-

sented in Table I. At four of the boilers, on-line
gas chromatographic measurements sponsored by
the U.S. EPA were made in parallel and showed
similar results.[13]

Natural Gas Firing:

The N$_2$O emission from three natural gas-fired
utility boilers ranging in size from 215 to 750 MW
were consistent with the previously reported re-
sults.[2] The N$_2$O emissions from these natural gas-
fired utility boilers were low, less than 2 ppm. Also,
as seen in Table I, there was no correlation with
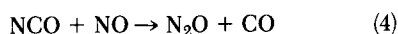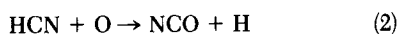the NO$_x$ emissions.

Residual Oil Firing:

The N$_2$O emissions from the two residual oil-fired
utility boilers (110 and 215 MW) were again low,
1 ppm, and exhibited no correlation with the NO$_x$
emissions.

Pulverized Coal Firing:

Seven pulverized coal-fired boilers were tested
ranging in size from 180 MW to 790 MW. As can
be seen in Table I, except for the 620 MW opposed
wall-fired boiler, the N$_2$O emissions were less than
6 ppm. The 12 ppm N$_2$O concentration measured
from the 620 MW opposed-fired unit may repre-
sent an upper limit on the emissions from this unit.
Because of the high SO$_2$ levels and NO$_x$ levels in
this flue gas, a small amount of N$_2$O may have
formed in the unheated sample lines during trans-
port to the analyzer.

Circulating Fluidized Bed Combustion:

N$_2$O emissions were also characterized at three
circulating fluidized bed combustors. Compared to
pulverized coal-fired boilers, the circulating bed units
exhibit elevated levels of N$_2$O emissions. At full load
operation of these units, N$_2$O levels ranged from 84
to 26 ppm (dry at 3% O$_2$).[14] The corresponding NO$_x$
levels varied from 81 to 283 ppm (dry at 3% O$_2$).[13]
At one of the units, tests were conducted over a
range of operating loads, from 55 to 100% of rated
load. A summary of this unit's emissions are pre-
sented in Table II. The N$_2$O and NO$_x$ levels are
plotted as a function of load in Figure 2a. For this
unit, the N$_2$O levels decrease and NO$_x$ increases as
the load increases. Further, for this unit the N$_2$O
and NO$_x$ emissions appear to correlate with bed
temperature (see Fig. 2b). The N$_2$O levels decrease
and NO$_x$ increases as the bed temperature in-
creases. The trends in N$_2$O concentrations with bed
temperature are consistent with the results ob-
tained from pilot-scale fluidized bed combustors re-
ported by Amand and Anderson[15] and the mecha-
nism suggested by Kramlich et al.[16] Kramlich et al.[16]
suggest that N$_2$O formation can occur from HCN
through a mechanism of the form

$$HCN + OH \rightarrow HNCO + H \qquad (1)$$

$$HCN + O \rightarrow NCO + H \qquad (2)$$

$$HNCO + OH \rightarrow NCO + H_2O \qquad (3)$$

$$NCO + NO \rightarrow N_2O + CO \qquad (4)$$

Peak conversion of HCN to N$_2$O via the above

TABLE I
N$_2$O emissions from full-scale utility combustion systems

Design Type	Fuel	Load (%)	NO$_x$* (ppm)	N$_2$O* (ppm)
Single Wall-Fired Boiler	Nat. Gas	98	120	2
Opposed-Fired Boiler	Nat. Gas	97	142	2
T-Fired Boiler	Nat. Gas	100	58	1
Single Wall-Fired Boiler	Resid. Oil	100	268	1
Single Wall-Fired Boiler	Resid. Oil	91	291	2
Opposed-Fired Boiler	Pulv. Coal	97	982	12
Opposed-Fired Boiler	Pulv. Coal	97	701	3
Opposed-Fired Boiler, Triple Cell	Pulv. Coal	98	692	6
T-Fired Boiler	Pulv. Coal	95	325	1
T-Fired Boiler	Pulv. Coal	82	390	1
T-Fired Boiler	Pulv. Coal	69	393	1
T-Fired Boiler	Pulv. Coal	51	498	1
Circulating Fluidized Bed	Crushed Coal	100	81	84

*Corrected to 3% O$_2$.

TABLE II
Emissions from the circulating fluidized bed combustor

Load % of Rated	T_{bed} °K	O_2 % dry	CO_2 % dry	CO ppm dry	SO₂ ppm corr	NO ected to 3%	N₂O O₂ dry
55	1116	5.0	14.6	127	86	55	126
75	1141	3.9	15.6	76	79	61	93
100	1146	3.6	16.0	86	81	81	84

mechanism occurs at a temperature of about 1250 K. Below 1250 K, N₂O concentrations are controlled by the formation of NCO and the conversion of NCO to N₂O. Above 1250 K, removal of N₂O through reactions with H and OH control the level of N₂O. At the circulating fluidized bed tested over a range of loads, bed temperatures ranged between 1116 and 1140 K, suggesting that the N₂O levels from this unit are controlled by formation processes rather than destruction reactions.

Further investigations are needed to assess what other operational variables yield higher or lower N₂O levels in CFBC's. While N₂O levels correlated with bed temperature for the unit where tests were conducted over a range of loads, all three of the units tested operated at similar bed temperatures at full load. Yet, the N₂O levels varied from 26 to 84 ppm. Other parameters that might influence the level besides temperature include the fuel type (char N evolution), char and/or solids loading, residence time, calcium species, sulfur species, and NO$_x$ level. Certainly the field data suggest there are operational conditions that minimize N₂O in CFBC's, offering possible keys to its control. Once the primary N₂O formation mechanisms are understood, potential control mechanisms can be developed.

Fig. 2. N₂O and NO$_x$ emissions versus load from a circulating fluidized bed combustor. (a. as a function of load; b. as a function of bed temperature).

Selective Non-Catalytic NO$_x$ Reduction: Urea Injection

A number of selective non-catalytic NO$_x$ reduction processes (SNCR) are currently under development for utilization in industry. These include injection of ammonia (NH₃), urea (NH₂CONH₂), or cyanuric acid ([HNCO]₃) at temperatures nominally between 1200 and 1500 K where the decomposition products react with NO$_x$. Caton and Siebers[17] reported bench-scale results showing N₂O as a product of the reaction between cyanuric acid and NO$_x$, presumably via reactions 3 and 4. Further, they suggested that urea injected into high temperature combustion products would decompose to NH₃ and HNCO.

N₂O measurements were also made at a unit using urea injection to reduce NO$_x$. The boiler is rated at 110 MW and was firing residual oil. A summary of the full load data is presented in Table III. The urea/NO$_x$ molar injection ratio was varied between 0.0 (baseline) and 0.6. Without urea injection, the baseline NO$_x$ and N₂O emissions were 291 and 1 ppm, respectively. As the amount of urea injection increased, the NO$_x$ level decreased, and the N₂O level increased. Over the range of urea injection rates tested (urea/NO$_x$ molar ratio of 0.2 to 0.6), between 11 and 13% of the NO$_x$ removed was converted to N₂O. Further work is needed to 1) verify these first measurements, 2) thoroughly characterize N₂O formation from SNCR processes, and 3) develop a better understanding of the basic N₂O formation chemistry.
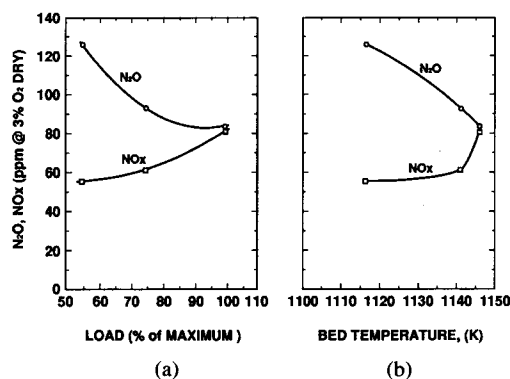
TABLE III
N₂O and NO$_x$ emissions: oil-fired boiler with urea injection

Urea/NO$_x$ (molar ratio)	NO$_x$ (ppm)	N₂O (ppm)	ΔNO_x (%)	$\frac{\Delta N_2O}{\Delta NO_x}$
0.0	291	1	—	—
0.2	206	10	29%	11%
0.4	161	16	45%	12%
0.6	117	23	60%	13%

Conclusions

The following conclusions can be drawn from the results discussed above:

- N$_2$O measurements using grab sampling techniques are subject to errors due to reactions between NO, SO$_2$, and H$_2$O forming N$_2$O in the sample containers. The N$_2$O formation occurs over a time period of 2–6 hours and depends on the amount of SO$_2$ initially present.
- Measurements using the continuous analyzer at a variety of conventional utility boilers (natural gas, residual oil, and pulverized coal-fired) indicate that direct N$_2$O emissions are low (generally, less than 6 ppm), and that the N$_2$O levels are not a substantial fraction of the NO$_x$ levels as previously suggested.
- Tests of circulating fluidized bed combustors yielded N$_2$O levels ranging from 26 to 84 ppm. The N$_2$O levels appear to be inversely related to the fluidized bed temperature.
- N$_2$O measurements at a full-scale boiler using urea injection for NO$_x$ reduction show that 11–13% of the reduced NO$_x$ is converted to N$_2$O.
- Further work is needed to determine if the chemistry occurring in the sample containers plays a role in increasing atmospheric N$_2$O concentrations; e.g., if NO$_x$, SO$_2$, and H$_2$O react in the atmosphere to form N$_2$O.

Acknowledgments

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