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Enhanced Effect of In-situ Generated Ammonium Salts Aerosols on the Removal of NO_x from Simulated Flue Gas

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The combined removal of sulfur dioxide (SO₂, up to 3000 ppm) and nitrogen oxides (NO and NO₂, up to 1200 ppm) has been investigated in a bench-scale pulsed-corona enhanced wet electrostatic precipitator (wESP) with the optional injection of ammonia and/or ozone. The reaction of ammonia with SO₂ produces submicron aerosols under certain conditions. Experiments have shown the feasibility of combined SO₂ and NO_x removal from simulated flue gases by the action of these in-situ generated aerosols. The mechanisms for NO_x removal include oxidation of NO to NO₂ and subsequent absorption of NO₂ into the water wall of the wESP. The results have shown that injecting NH₃ (NH₃/NO_x molar ratio 1) resulted in NO_x removal of ~13% in a simulated combustion flue gas. Injecting 200 ppm ozone (no ammonia) increased NO conversion to 35% by oxidation, but total NO_x removal increased to only 17%. Without the formation of ammonium salts aerosols (e.g., without SO₂ in the gas), co-injection of ammonia and ozone increased NO conversion to 60% and NO_x removal to 40%. However, high NO_x removals were measured in simulated flue gas that contained NH₃, SO₂, and ozone. The total NO_x removal efficiency was 79% when the ammonium salts aerosols were formed in the presence of 2400 ppm SO₂, 312 ppm O₃, and 2900 ppm NH₃. The energy efficiency of collection improved by ~250% for SO₂ removal and more than 4700% for NO_x removal under these conditions. It was determined that the ammonium salts aerosols produced from the reaction of ammonia and sulfur dioxide substantially enhanced total NO_x removal.

Introduction

The economical removal of NO_x and SO_x still represents a significant technical challenge that could ultimately determine the extent of the use of certain types of fossil fuels for energy production. A portion of the submicron aerosol formation in the atmosphere is directly related to the concentrations of these compounds. Pulsed corona technology has been developed as an alternative postcombustion

cleaning technology for the control of many gaseous pollutants, including NO_x, SO_x, mercury vapor, Freon, and other organic compounds. The reported removal mechanisms include electron attachment, oxidation by ozone or radicals, decomposition and reduction, and enhanced mass transfer.

Experiments conducted in our laboratory have shown the feasibility of SO_x, NO_x, and mercury removal in a pulsed-corona wet electrostatic precipitator (wESP) (1, 2). This paper presents the results of enhanced NO_x removal by the action of in-situ ammonia–sulfur aerosols for combined NO_x and SO_x removal. A major advantage of wESPs over dry systems is that there is no dust layer accumulation, especially for liquid aerosols or highly hygroscopic aerosols, tars, and oil mists contained in flue gases. Therefore, back-corona, spark-over, and dust re-entrainment can be avoided. In addition, wESPs experimentally perform better than dry ESPs in the removal of NO_x (3) because the chemical reactions involving water and its radicals help in the removal of NO_x (4).

Role of Ammonia in SO₂ Removal. Commercial developments in the late 1990s suggested the use of an ammonia (NH₃) reagent in conventional wet flue gas desulfurization (FGD) in a position downstream of an ESP (5, 6). The ammonia byproduct, mainly ammonium sulfate (NH₄)₂SO₄, when mixed with ammonia nitrate and a small portion of collected fly ash, is acceptable as an agricultural fertilizer containing both nitrogen and sulfur compounds, which is especially ideal for high alkaline soils. Sulfur-containing fertilizers are becoming more popular because larger crop yields have been removing increased amounts of sulfur from soils, and the continued use of non-sulfur fertilizers (6, 7) has not replenished these amounts of sulfur. Thus, with this usable byproduct, the system can be designed to be free from effluent generation (zero-effluent operation).

When NH₃ is injected into a flue gas that contains H₂O and SO₃ or SO₂, ammonia–sulfur aerosols are formed as small aerosol particles with a mass mean diameter of ~0.14 μm at room temperature (8). Various products may form depending on the reactant concentrations, moisture content, and the reaction temperature. The major products of NH₃ and SO₂ reactions are identified by X-ray diffraction to be ammonium sulfate crystals under excess moisture conditions from room temperature to 54 °C (9, 10). Both bench scale and pilot plant tests have shown that complete removal of sulfur dioxide is feasible at low temperatures (<50 °C), and the removal efficiency is in excess of 95% for temperatures below 85 °C for 2:1 molar injection ratios of NH₃/SO₂ (11–14). Both O₂ and NO enhance the formation of ammonium sulfate (15). With corona discharge, SO₂ removal is governed mainly by the thermo–chemical reactions with ammonia and enhanced by the corona process (16). Higher SO₂ removal efficiency has been obtained with less NH₃ usage under corona discharges, indicating that the thermo-stability of the byproduct is enhanced by the corona (17).

Ammonia injection has other advantages. Flue gas conditioning with ammonia can reduce the resistivity of fly ash as well for improved ESP performance. Ammonia is also the most successful material tested for the prevention of acid condensation because it diffuses rapidly and reacts immediately with SO₃ in flue gas environments (18).

Role of Ammonia in NO_x Removal. For NO_x removal, ammonia is widely used in conventional selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) processes as a reducing agent. In the electron beam method, amidogen radicals (NH₂), which are formed from ammonia or urea, are the primary reducing agents (19). In the presence

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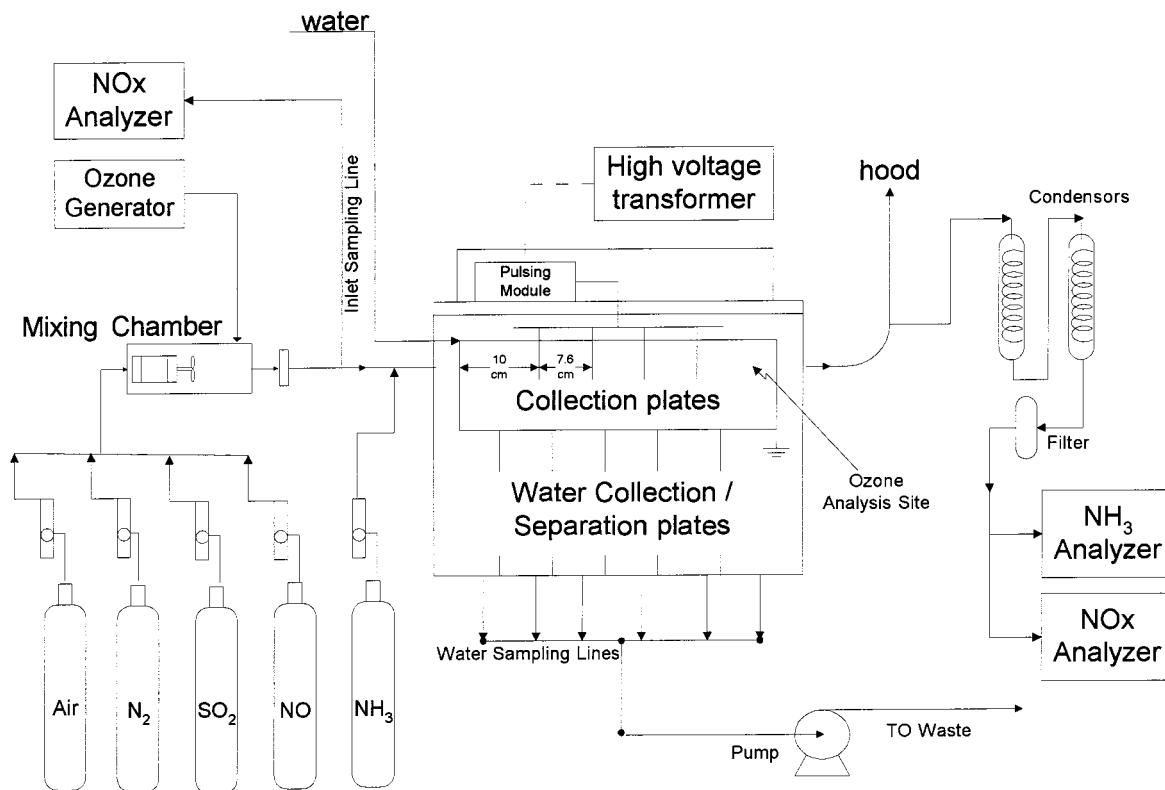


FIGURE 1. Overview of wESP system.

of oxidizing agents such as $\text{O}\cdot$ and $\text{OH}\cdot$ radicals, $\text{NH}_2\cdot$ radicals convert NO_x into ammonium nitrate aerosols (20, 21). However, the decomposition of ammonia is not observed in pulsed corona discharge processes because of the low electron energy level (22).

Ammonia enhances the removal of NO_2 by forming ammonium salts. Ammonia does not enhance the removal of NO , because there is no direct reaction between NH_3 and NO at room temperature (22). Mizuno et al. (3) showed that in a dry ESP at temperatures up to 150°C , ammonia effected only NO_2 removal, but not NO removal. This is because the conversion of NO to NO_2 does not depend on ammonia but mainly on the concentration of free oxygen radicals (23). With ammonia and water vapor, both NO and NO_x removal efficiencies are enhanced proportional to the temperature and corona power, because NO is oxidized to NO_2 by $\text{OH}\cdot$ formed from water vapor (3).

Wet ESPs with NH_3 injection have achieved better NO_x removal with the addition of ammonia and water vapor (3, 4), which is similar to the reported results with dry ESPs (20). NO_x is converted mainly to NH_4NO_3 aerosols in a streamer corona with the presence of ammonia (23, 24). It was confirmed by infrared spectroscopy that NH_4NO_3 is the final product of the $\text{NO}_x/\text{NH}_3/\text{H}_2\text{O}$ reaction in the presence of a corona discharge (4).

Ammonia may be used for SO_2 and NO_x removal to either form aerosols or neutralize the sulfurous and nitrous acids produced in coronas. Because there is competition between NO_2 and SO_2 for the ammonia, SO_2 is effectively removed only after NO_2 has been removed (22). Onda et al. (24) conducted experiments on $\text{NO}_2/\text{SO}_2/\text{NH}_3/\text{H}_2\text{O}$ mixtures in a simulated flue gas with a dry pulsed corona. The composition of the collected material was 49 mol % of $(\text{NH}_4)_2\text{SO}_4$ and 47 mol % of $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$. These byproducts were solid and soluble in water and were easily removed from the gas stream.

Experimental Section

A wESP system was used to measure SO_2 and NO_x removal in a continuous flow system as shown in Figure 1. The wESP consisted of a mixing chamber, inlet and outlet ducts, a collecting area in the top section for NO_x removal studies, and a bottom section for the collection and sampling of the water. From an air pollution control standpoint, the wESP system combines the advantage of a wet FGD system with the use of NH_3 reagent, while the electrostatic function efficiently collects ammonium aerosols and acid mist. In addition, the corona discharge aids in the oxidation of the SO_2 and NO to SO_3 and NO_2 , so more byproducts are in the stable sulfate and nitrate form rather than in the unstable sulfite form.

Pure SO_2 and NO were mixed with laboratory compressed air or pure nitrogen in the mixing chamber. In addition, air–nitrogen– CO_2 mixtures with 70% relative humidity were made to simulate 3%- and 6%- O_2 flue gases with 11% CO_2 . Airflow rates ranged from 75 to 132 L/min (ideal gas residence times from 8.6 to 15 s) with initial SO_2 concentrations of 1000–3000 ppm and NO concentrations of 400–1000 ppm. The top part of the wESP contained the electrode wires and the grounded collection plates. Plate-to-plate spacing was 20.3 cm, with discharge electrode wires spaced 10 cm from the inlet and outlet and 7.6 cm apart. Pressure inside the top box was slightly higher than atmospheric pressure to prevent dilution from outside air. The gas mixture passed through the electrode chamber and the pollutants were collected by the water film running uniformly over the grounded plates with a water flow rate 3.8 L/min.

Inlet and outlet SO_2 concentrations were continuously sampled by SO_2 analyzers (PIR-2000 and VIA-300 NDIR, Horiba Instruments, Inc., Irvine, CA), and NO and NO_x concentrations were continuously sampled by a chemiluminescence $\text{NO}-\text{NO}_x$ analyzer (Thermo Environmental Instruments 42H analyzer). The reading of total NO_x includes

TABLE 1. Summary of Maximum Removal Efficiency in Air and in Simulated Flue Gas in the wESP^a

	without in situ ammonium salts aerosols				with in situ ammonium salts aerosols			
	pulsed wESP	with NH ₃ injection		with O ₃ injection	with NH ₃ + O ₃ co-injection		with NH ₃ + O ₃ co-injection	
corona discharge	30 kV	30 kV	30 kV	30 kV	30 kV	30 kV	40 kV	40 kV
NH ₃ injection	0	2500 ppm	5800 ppm	0	2500 ppm	5800 ppm	2900 ppm	5800 ppm
O ₃ injection	0	0	0	200 ppm	200 ppm	200 ppm	312 ppm	312 ppm
maximum SO ₂ removal	50~55%	88~95%	98~100%	76~79%	~98%	~99%	~100%	~100%
NO _x Removal In Air								
maximum NO oxidation	28%	32%	n.a.	57~59%	64~67%	n.a.	n.a.	n.a.
maximum total NO _x removal	18%	25%	n.a.	39~43%	51~57%	n.a.	n.a.	n.a.
NO _x Removal In Flue Gas (3% O ₂)								
maximum NO oxidation	6%	n.a.	14%	36%	74%	80%	82%	78~80%
maximum total NO _x removal	5%	n.a.	13%	17%	72%	79%	77%	72~76%

^a Experiments were conducted in air or in 3% O₂, 11% CO₂ humidified simulated flue gas at 25 °C, with ~700 ppm NO, ~2400 ppm SO₂, 8.6 s gas residence time, 3.8 L/min 12 °C water, with 30~40 W pulsed coronas.

the concentrations of NO, NO₂, and other nitrogen oxides. Ozone was generated by an ozone generator (Welsbach ozonator MD408) and continuously measured at the end of the collection plates by an ozone analyzer (1003AH, Dasibi Environmental Corp., Glendale, CA). Ammonia injection was 53 cm upstream of the corona region (collection plates). The outlet ammonia concentration was sampled continuously 20 cm downstream of the corona region (PIR-2000, Horiba Instruments, Inc., Irvine, CA).

A chiller-filter system was installed in the gas sampling line to improve the accuracy of the measurements. Two condensers were used to promote condensation, and traps and filters removed condensed moisture and aerosols to prevent water and fine aerosols from entering the analyzers. The collected aerosols were analyzed for carbon, hydrogen, nitrogen, and sulfur contents (Leco CHNS-932, Leco Corp., St. Joseph, MI).

A high-voltage transformer produced positive or negative DC corona discharge (Series WK, Glassman High Voltage, Inc.). Because of the limitation of spark over, the maximum achievable voltage level in the system was ~60 kV. Previous studies have shown that pulsed coronas exhibit higher removal efficiencies of NO_x or SO_x than DC coronas (16, 22). Therefore, a pulsing module (90 Hz) driven by a variable-speed motor was added. Pulsing increased the obtainable power level without undue sparking.

Results and Discussion

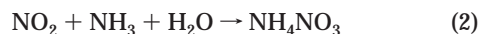
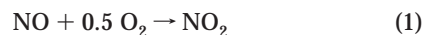
The proposed reaction paths are the oxidation of NO followed by the formation of ammonium salt aerosols. The aerosols are subsequently charged and separated by the electrical field and removed from the system by water. Therefore, the experimental results are expressed as the oxidation of NO to NO₂ and the removal of total NO_x from the gas phase.

Without Ammonia-Sulfur Aerosols. *Without Ammonia or Ozone Injection.* Previous results (1, 2) without ammonia or ozone injection showed that both NO_x and SO₂ removal efficiency increased with gas residence time, inlet concentration, and applied corona power. Without NH₃ injection, SO₂ can be easily removed up to 40% by the water film and removed further to 70% by 60 kV corona discharge in the wESP. Ammonia injection improved the SO₂ removal to ~100%. In the wESP, removing SO_x requires less energy than removing NO_x, and is not a function of the O₂ level of the flue gas.

Table 1 summarizes the results of the experiments. In a pure N₂ stream, NO was not affected by a 31 kV corona discharge, or by the presence of water in the wESP. These

results suggest that NO_x removal can be initiated only after NO is oxidized by either O₂, O₃, or the oxidizing radicals developed from O₂ under the corona discharge. In an air stream, NO_x removal efficiency was limited to ~20% when the gas residence time was less than 8.5 s. In the simulated flue gas, NO_x removal efficiency dropped from 20% (in air) to 5% (in 3%-O₂ flue gas) and 12% (in 6%-O₂ flue gas) due to the change in oxygen level. Corona discharge enhanced SO₂ removal, but not NO_x removal. When a corona was applied to the simulated flue gas, the improvement of NO_x removal efficiency was less than 3% at 60 kV.

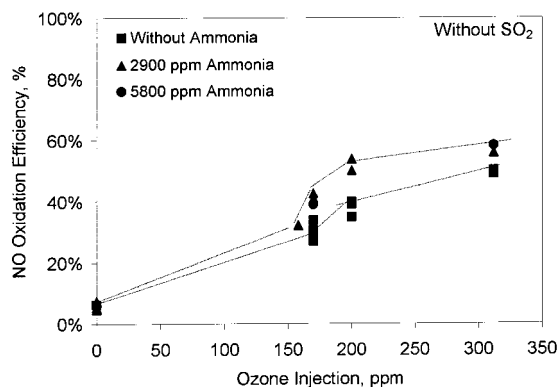
With Ammonia Injection Only. With ammonia injection only, SO₂ removal quickly approached ~100% and white aerosols were instantly formed. In a simulated flue gas, the corona only oxidized 2~3% NO to NO₂ which then subsequently reacted with NH₃. This is illustrated in eqs 1 and 2:



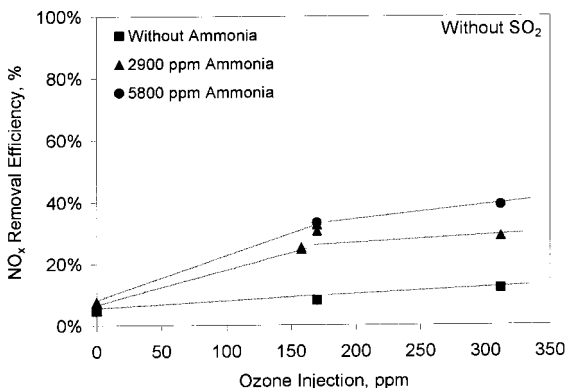
The NH₃ increased NO_x removal by only 2~3% at a NH₃-NO_x molar ratio of 1, and only ~8% at a molar ratio of 8 (Table 1). The reaction rate of NH₃ with NO is insignificant compared to that of NH₃ with NO₂. Increasing the oxygen level from 3% to 6% resulted in ~5% additional NO_x removal efficiency.

With Ozone Injection Only. The low oxygen content in the flue gas (3~6%) did not result in sufficient NO oxidation to achieve a significant level of NO_x removal. Also, the corona voltage (maximum of 60 kV) in the wESP was not enough to drive a significant chemical reaction to oxidize NO. Therefore, ozone was injected into the simulated flue gas as an oxidizer. The injection of 200 ppm O₃ increased SO_x removal to 80% (Table 1), which is attributable to increased formation of SO₃, which is extremely hygroscopic.

In air (without NH₃ injection), the injection of 200 ppm ozone greatly improved NO oxidation to 50~58% as determined by the increase in the NO₂ concentration, which resulted in total NO_x removal of 41% (Table 1). The byproducts of NO oxidation by ozone are mainly NO₂ and N₂O, as reported in the literature (4). However, the extent of the production of N₂O depends on the residence time, and its production decreased to zero at short residence time in a semi-wet reactor (4). The enhanced mechanisms of ammonia-sulfur aerosols proposed in this paper should effectively convert most NO₂ and N₂O to ammonium nitrate. Ozone oxidation of NO can result in the formation of other



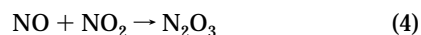
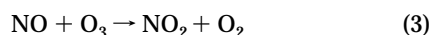
(a) NO Oxidation



(b) NO_x Removal

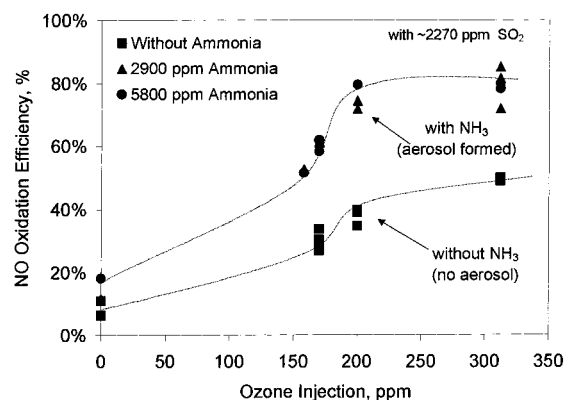
FIGURE 2. NO_x removal enhancement by ammonium and ozone injection (without SO₂). Wet ESP experimental conditions: in 25 °C 3% O₂, 8~11% CO₂ humidified simulated flue gas, with 700~800 ppm NO (750~850 ppm NO_x), without SO₂, 8.6 s gas residence time, 3.8 L/min 12 °C water, with 30~40 kV negative pulsed corona.

NO_x compounds such as N₂O₃, which is illustrated in eqs 3 and 4:

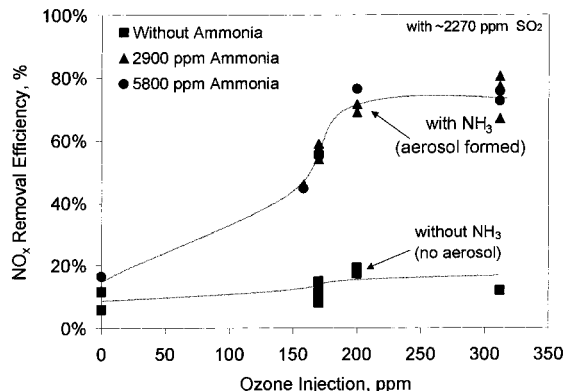


However, from our results in a simulated flue gas (reduced O₂ concentration), ozone injection increased NO oxidation from 6% to 36%, but increased total NO_x removal only from 5% to 17%. The absorption capacity of NO₂ in water (Henry's constant 0.01 mol/L-atm) is higher than that of NO (0.0019 mol/L-atm), but still much lower than that of SO₂ (1.24 mol/L-atm). These results indicate that within the short gas residence time, NO₂ cannot be removed efficiently in the wESP by simple absorption.

With Ammonia and Ozone Co-Injection. To separate the effects of the in-situ ammonium salts aerosols, experiments in this section were conducted in the absence of SO₂. NH₃ injection resulted in minor amounts of NO oxidation (Figure 2a), and no further improvement was measured when NH₃ injection was doubled. The injection of 312 ppm ozone resulted in the oxidation of 60% of the NO into NO₂ (Figure 2a and Table 1); the NO₂ subsequently reacted with NH₃ to form NH₄NO₃ aerosols (visually confirmed), which increased NO_x removal efficiency. Higher NH₃ concentrations produced more NH₄NO₃ aerosols, which resulted in more NO₂ and total NO_x removal. The maximum NO_x removal was 40% because of the formation of NH₄NO₃ aerosols with a high NH₃ injection rate (NH₃ to NO_x molar ratio 7.25).



(a) NO Oxidation



(b) NO_x Removal

FIGURE 3. Improved NO_x removal enhancement by ammonium and ozone injection (with SO₂). Wet ESP experimental conditions: in 25 °C 3% O₂, 8~11% CO₂ humidified simulated flue gas, with 700~800 ppm NO (750~850 ppm NO_x), 2200~2500 ppm SO₂, 8.6 s gas residence time, 3.8 L/min 12 °C water, with 30~40 kV negative pulsed corona.

Enhanced Effect of In-situ Ammonia–Sulfur Aerosols.

Very high NO_x removals were measured when in-situ ammonium salts aerosols were formed in a simulated flue gas that contained ammonia, sulfur dioxide, and ozone. Table 1 summarizes these results, which are shown graphically in Figures 3a and 3b. Injecting 200 ppm ozone and 2900 ppm NH₃ (NH₃ to SO₂ + NO_x molar ratio 0.94), NO and NO_x removal were 72%. Further increasing the additives to 312 ppm O₃ and 5800 ppm NH₃ (molar ratio 0.88), total NO_x removal increased to 80%. Because the amount of input NH₃ (2900 ppm) is about the sum of the removed SO₂ and NO_x (98% of 2400 ppm SO₂ and 72% of 700 ppm NO_x), the formed ammonium salt aerosols were more likely to be ammonium bi-sulfite (NH₄HSO₃) or bi-sulfate (NH₄HSO₄), along with ammonium nitrate (NH₄NO₃). The agreement between NO oxidation and NO_x removal in Figure 3 indicated that most NO₂ was removed when ammonia–sulfur aerosols were formed. It appears that the surface of the ammonium salts aerosols acted as a site where additional adsorbed NO₂ and NH₃ could react.

The ammonium salts aerosols improved not only NO₂ removal, but also NO oxidation. The formation of NH₄NO₃ increased NO oxidation by 10 ~ 15% (Figure 2a), whereas the formation of ammonium salts aerosols increased NO oxidation by 30 ~ 40% (Figure 3a). The improved utilization of ozone suggests that NO and O₃ molecules can be adsorbed to the surface of the aerosols as well.

The enhanced effect of the in-situ ammonium salts aerosols was verified by adjusting the amount of aerosol formation as shown in Figure 4. With a constant ammonia

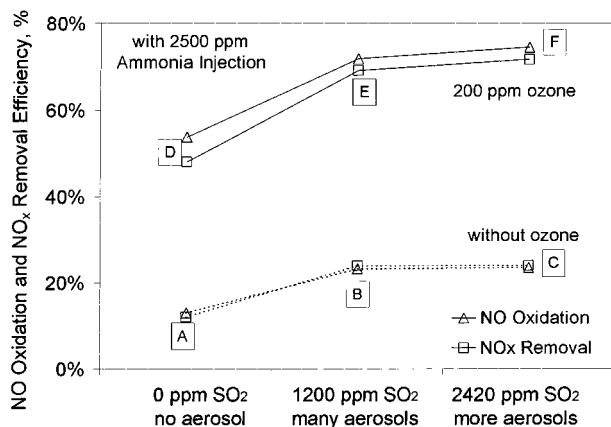


FIGURE 4. Amount of ammonium salt aerosols improve the NO_x removal efficiency. Wet ESP experimental conditions: for 200-ppm-O₃ tests, in 4.3% O₂ simulated flue gas; for without-O₃ tests, in 6% O₂ simulated flue gas; for all tests, in 25 °C 8% CO₂ humidified simulated flue gas, 700 ppm NO, 8.6 s gas residence time, 3.8 L/min 12 °C water, with a positive pulsed corona.

injection rate for all tests, more SO₂ resulted in more in-situ aerosols, which increased both the NO oxidation and NO_x removal.

The role of ozone is also significant. In the experiments without ozone (Figure 4), the enhanced effect of aerosols was limited (~10%, point A to C). With 200 ppm ozone, the enhanced effect of aerosols was ~25% (point D to F). These results can also be determined from Figures 2a and 3b where the effect of ozone concentration on NO oxidation is strongly apparent. Therefore, a strong oxidizer such as ozone is necessary in the proposed denitrification process.

The mechanisms of NO oxidation and NO_x removal are summarized and illustrated in Figures 5a, 5b and 5c. Oxidation of NO by oxygen in the flue gas was consistently low, and around 5% for all cases. Figure 5a summarizes the results without the presence of SO₂ or NH₃ in air. The corona discharge improves NO oxidation and total NO_x removal, but not substantially. The injection of ozone further improves NO oxidation and NO_x removal, but not to high levels. Figure 5b illustrates the impact of ammonium salts aerosols on total NO_x removal in a simulated flue gas when the ammonia-sulfur dioxide concentrations are approximately equal. With the presence of these aerosols, the total NO_x removed was ~70%. When an excess of NH₃ was injected, the results are as shown in Figure 5c. Here, very high levels of NO oxidation and NO_x removal were measured. It is believed the in-situ ammonium salts aerosols serve as highly efficient adsorbents with tremendous surface area and enhance the chemical reactions of NO_x removal. The complete reaction pathway is unknown, but it is postulated that ozone, NO, H₂O, and NH₃ were adsorbed to the surface of the ammonia-sulfur aerosols, which resulted in the oxidation of NO and formation of NH₄NO₃. The ammonia-sulfur aerosol formation step itself is a SO₂ removal process that improved SO₂ removal to ~100%. Once the SO₂ and NO_x are separated from the gas, all the pollutants and byproducts are trapped on the aerosol surface and reverse reactions are greatly hampered (22). Any un-reacted gas pollutants absorbed on the surface are removed with the aerosols. After the SO₂ and NO_x are separated from the gas phase, the final products, ammonium salt aerosols, can be removed by conventional particle removal equipment such as an electrostatic precipitator or a bag house. The high collection efficiency of aerosols in the wESP was visually confirmed in our system.

Ultimate Analysis of the Ammonium Aerosols. As mentioned in a previous section, the formed ammonium salt aerosols were more likely to be ammonium bi-sulfite

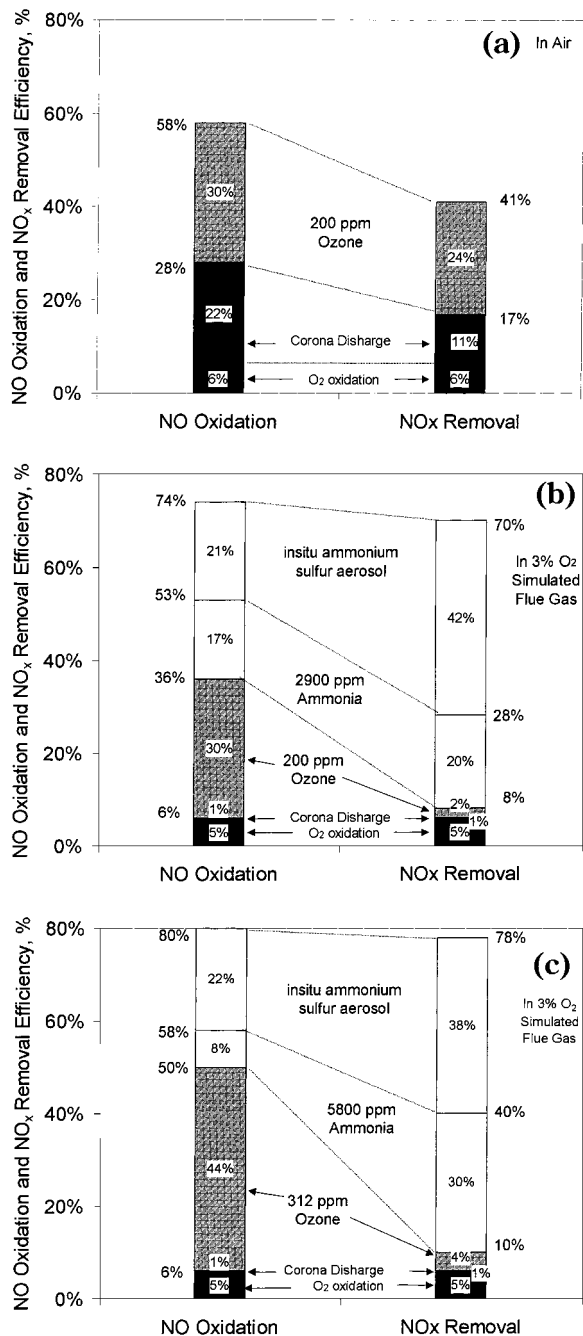


FIGURE 5. Mechanisms of NO oxidation and NO_x removal in air and simulated flue gas. (a) In air, wet ESP experimental conditions: in 25 °C 43% RH air, 800~1000 ppm NO, 8.6~10 s gas residence time, 3.8 L/min 10 °C water, with a positive pulsed corona. (b) In simulated flue gas, wet ESP experimental conditions: in 25 °C 3% O₂, 8~11% CO₂, humidified simulated flue gas, 800~1000 ppm NO, 2500 ppm SO₂, 10 s gas residence time, 3.8 L/min 10 °C water, with pulsed coronas. (c) In simulated flue gas with more additives, wet ESP experimental conditions: in 25 °C 3% O₂, 8~11% CO₂, humidified simulated flue gas, 800~1000 ppm NO, 2500 ppm SO₂, 10 s gas residence time, 3.8 L/min 10 °C water, with pulsed coronas.

(NH₄HSO₃) or bisulfate (NH₄HSO₄), along with ammonium nitrate (NH₄NO₃). This was confirmed by an analysis of the collected aerosols for C, H, and N contents and a total sulfur analyzer for the sulfur content. The oxygen content was estimated by assuming the remaining content is oxygen.

For wESP experiments in which the NH₃ was injected at a rate to include one mole of NH₃ for the molar sums of SO₂ and NO (with results of 98% SO₂ removal and 72% NO_x

removal), the byproducts consisted of 0.1 ~ 3% carbon, 1.5 ~ 1.7% hydrogen, 15 ~ 18% nitrogen, and 17 ~ 26% sulfur. The small amounts of carbon were due to minor amounts of $(\text{NH}_4)\text{HCO}_3$ formation. Considering all the possible compounds (ammonium nitrate, sulfite, bi-sulfite, sulfate, and bisulfate), the constituent composition of the solid byproducts was estimated by minimizing the squares of the differences of the C, H, N, S, and O values. The best-fitting combination of constituent composition was 80.5% $(\text{NH}_4)\text{HSO}_4$, 12.3% NH_4NO_3 , 5.7% H_2O , and 1.5% $(\text{NH}_4)\text{HCO}_3$. This suggests that most of the SO_2 and NO_x were ultimately converted to NH_4HSO_4 and NH_4NO_3 , respectively.

Also, during the experiments, we measured the amount of ammonia that remained un-reacted and exited the system (i.e., "ammonia slip"). Ammonia slip is always an environmental concern, especially with regard to submicron aerosol formation in the atmosphere. Although high amounts of NH_3 were injected into the system, the outlet NH_3 concentration was always below the detection limit (100 ppm) of the ammonia analyzer whenever ammonium salt aerosols were formed. Future research is required to minimize the amount of ammonia slip with respect to the degree of NO oxidation. However, it is anticipated that low NH_3 emissions can be achieved because of the following three reasons. 1. Because of the high rate of reaction of NH_3 with SO_2 , the NH_3 input rate should be kept at levels equal to or less than the stoichiometric ratio required (NH_3 to SO_2 and NO_x). 2. NH_3 is soluble, and unreacted NH_3 easily dissolves into the water of the wESP (the solution should be maintained at a high pH level before treatment in order to prevent NH_3 from being released back to the air). 3. The corona discharge further enhances NH_3 absorption similar to that of SO_2 absorption in the wESP.

Therefore, the following significant advantages over conventional technology can be concluded from these results:

1. Simultaneous removal of NO_x and SO_x could be achieved in a single pollution control device such as a wet ESP, which requires a smaller installation space and investment costs than conventional combinations of FGD and catalytic NO_x removal processes.

2. High NO_x removal efficiency (~80%) can be reached by the presence of in-situ ammonium salts aerosols.

3. High sulfur coal is not detrimental. SO_2 is not only removed up to levels of ~100%, but also used as a source of the ammonium salts sorbent. Although ammonia is needed for the formation of the sorbent, only SO_2 is consumed. Ammonia could be recycled from the solution.

4. The costs associated with the corona energy are reasonable. Without O_3 or NH_3 injection, the maximum removals for SO_2 and NO_x were approximately 70% and 5%, respectively (with the experimental conditions 1888 cm^3/sec gas flow rate, 60 W primary corona supply, room temperature, 1 atmospheric pressure, in a simulated flue gas). The calculated energy efficiency of SO_x and NO_x removals for these conditions are 681 $\text{g}_{\text{SO}_x}/\text{kW-hr}$ and 8 $\text{g}_{\text{NO}_x}/\text{kW-hr}$. With 312 ppm O_3 and 2900 ppm NH_3 injection, however, the maximum removals for SO_2 and NO_x were ~99% and 77% respectively (at 2017 cm^3/sec gas flow rate, 11.3 W primary corona supply plus 8.14 W O_3 generation). The energy efficiencies of SO_x and NO_x removals are as high as 2360 $\text{g}_{\text{SO}_x}/\text{kW-hr}$ and 385 $\text{g}_{\text{NO}_x}/\text{kW-hr}$ (without considering the energy for injection). The chemical reactions with O_3 and NH_3 and the enhanced effect of ammonia aerosols greatly increased the utilization of energy.

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Literature Cited

- (1) Tseng, C. H.; Keener, T. C.; Khang, S. J.; Lee, J. Y. *Adv. Environ. Res.* **1999**, 3 (3), 309.
- (2) Tseng, C. H.; Keener, T. C.; Khang, S. J. In *Proceedings of the Air & Waste Management Association's 92nd Annual Meeting*, St. Louis, MO, June 1999; AWMA: Pittsburgh, PA, 1999.
- (3) Mizuno, A.; Shimizu, K.; Matsuoka, T.; Furuta, S. *IEEE Trans. Ind. Appl.* **1995**, 31 (6), 1463.
- (4) Chakrabarti, A.; Mizuno, A.; Shimizu, K.; Matsuoka, T.; Furuta, S. *IEEE Trans. Ind. Appl.* **1995**, 31, 500.
- (5) Brown, G. N. *Ammonia Scrubbing Makes High Sulfur Fuels Economical*, Marsulex Environmental Technologies, Lebanon, Pennsylvania, 1999.
- (6) Ellison, W. *24th International Technical Conference on Coal Utilization and Fuel Systems*, Clearwater, FL, Presented by the Coal & Slurry Technology Association and the American Society of Mechanical Engineers' Fuels and Combustion Technologies Division, in cooperation with the U.S. Department of Energy's Pittsburgh Energy Technology Center: Coal and Slurry Technology Association, Washington, D.C., Mar 1999.
- (7) Borio, D.; Rader, P.; Walters, M. *Ammonia Scrubbing: Creating Value from SO_2 Compliance*, ABB Environmental Systems: Knoxville, TN, 1999.
- (8) Bai, H. Ph.D. Dissertation, The University of Cincinnati, Cincinnati, OH, 1992.
- (9) Hartley E. M.; Matteson M. J. *Ind. Eng. Chem. Fundam.* **1975**, 14, 67.
- (10) Stromberger, M. J. MS Thesis, University of Cincinnati, Cincinnati, OH, 1984.
- (11) Shale, C. C. *Pollution Control and Energy Needs, Advances in Chemistry Series 127*, American Chemical Society: Washington, DC, 1973, p 195.
- (12) Shale, C. C.; Simpson, D. G.; Lewis, P. S. *Important Chemical Reactions in Air Pollution Control*; *Chem. Eng. Prog., Symp. Ser.* **115**, **1971**, 67, 52.
- (13) Davis, W. T.; Keener, T. C.; Means, C. S.; Dooley, R. P. *70th Annual Meeting of the Air Pollution Control Association*, June 1977; Paper 77-26.3, The Air Pollution Control Association, Pittsburgh, PA.
- (14) Keener, T. C.; Davis W. T. *Demonstration of a $\text{Ca}(\text{OH})_2/\text{NH}_3$ Based System For Removal of SO_2 on High Sulfur Coals*; Final Report to the Ohio Coal Development Office on Grant OCDO R-86-79; OCDO, Ohio Department of Development: Columbus, OH, 1988.
- (15) Hirota, K.; Makela, J.; Tokunaga, O. *Ind. Eng. Chem. Res.* **1996**, 35, 3362.
- (16) Dinelli, G.; Civitano, L.; Rea, M. *IEEE Trans. Ind. Appl.* **1990**, 26 (3), 535.
- (17) Ning, C. et al. *Huanjing Kexue (Environmental Science)* **1994**, 15 (1), 15.
- (18) Rendle, L. K., and Wilsdon, R. D. *Combustion* **1957**, 30.
- (19) Boyle, J.; Russell, A.; Yao, S. C.; Zhou, Q.; Ekmann, J.; Fu, Y.; Mathur, M. *Fuel* **1993**, 72 (10), 1419.
- (20) Chang, J. S.; Lawless, P. A.; Yamamoto, T. *IEEE Trans. Plasma Sci.* **1991**, 19 (6), 1152.
- (21) Masuda, S. *4th International Conference on Electrostatic Precipitation*; Air Pollution Control Association: Pittsburgh, PA, 1990; Chapter 9, p 615.
- (22) Masuda, S.; Nakao, H. *IEEE Trans. Ind. Appl.* **1990**, 26 (2), 374.
- (23) Chang, J. S. *J. Aerosol Sci.* **1989**, 20 (8), 1087.
- (24) Ohkubo, T.; Kanazawa, S.; Nomoto, Y.; Chang, J. S.; Adachi, T. *IEEE Trans. Ind. Appl.* **1994**, 30 (4), 856.
- (25) Onda, K.; Kasuga, Y.; Kato, K.; Fujiwara, M.; Tanimoto, M. *Energy Convers. Manage.* **1997**, 38, 1377.

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