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Removal of SO_2 and the Simultaneous Removal of SO_2 and NO from Simulated Flue Gas Streams Using Dielectric Barrier Discharge Plasmas

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A gas-phase oxidation method using dielectric barrier discharges (DBDs) has been developed to remove SO_2 and to simultaneously remove SO_2 and NO from gas streams that are similar to gas streams generated by the combustion of fossil fuels. SO_2 and NO removal efficiencies are evaluated as a function of applied voltage, temperature, and concentrations of SO_2, NO, $H_2O_{(g)}$, and NH_3. With constant $H_2O_{(g)}$ concentration, both SO_2 and NO removal efficiencies increase with increasing temperature from 100 to 160°C. At 160°C with 15% by volume $H_2O_{(g)}$, more than 95% of the NO and 32% of the SO_2 are simultaneously removed from the gas stream. Injection of NH_3 into the gas stream caused an increase in SO_2 removal efficiency to essentially 100%. These results indicate that DBD plasmas have the potential to simultaneously remove SO_2 and NO from gas streams generated by large-scale fossil fuel combustors.

KEY WORDS: Dielectric barrier discharge; SO_2 removal; NO removal; gas-phase oxidation.

1. INTRODUCTION

SO_2 and NO_x (including NO and NO_2) have been known to be gaseous air contaminants for decades. They have adverse effects on human health,[1] damage vegetation,[2] and degrade materials.[3] SO_2 and NO are also the

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two most important gaseous air contaminants that contribute to acid rain which has had detrimental effects on ecosystems in North America and Europe.[4] In addition, SO_2 and NO contribute to the degradation of visibility since they form accumulation-mode aerosol particles containing sulfates and nitrates.[5,6] Furthermore, NO chemically reacts with gaseous hydrocarbons in the atmosphere to form noxious photochemical contaminants such as O_3 and peroxyacetyl nitrate (PAN).[7] In recent years, the degradation of visibility at some national parks in the United States and the widespread failure to satisfy the National Ambient Air Quality Standards for O_3 in large metropolitan areas such as Los Angeles and Chicago have caused public concern.[8,9]

As the emission standards for SO_2 and NO_x become more stringent as described in the 1990 Clean Air Act Amendments, the cost to achieve these standards also escalates. Given the constraints of current technology for removing SO_2 and NO from gas streams, it would be useful to simultaneously remove SO_2 and NO from gas streams in a single process that is not as complicated or expensive as existing technology. Gas-phase oxidation processes using electron beams (e-beams) have been demonstrated as an effective technology to simultaneously remove SO_2 and NO from gas streams.[10-12] With NH_3 injection, removal efficiencies for SO_2 (η_{SO_2}) and NO (η_{NO}) were over 90 and 80%, respectively.[13] Nevertheless, the high cost and potential X-ray hazard of the process have motivated research to develop more effective gas-phase oxidation processes.

This paper discusses dielectric barrier discharge (DBD) plasmas, also known as silent discharges, as an innovative gas-phase oxidation process that simultaneously removes SO_2 and NO from gas streams. This process uses DBDs to generate gas phase radicals, such as hydroxyl (OH), hydroperoxyl (HO_2), and oxygen atom (O), that simultaneously oxidize SO_2 and NO to form particles consisting of H_2SO_4 and HNO_3, respectively. The particles can then be chemically neutralized with NH_3 to form $(NH_4)_2SO_4$ and NH_4NO_3. In an industrial application of this process, the particles could then be removed from the gas stream by a particle removal device, such as a fabric filter or electrostatic precipitator.[14] A DBD was chosen for this study because of its relatively low cost and high efficiency at generating gas-phase radicals.[15]

2. GAS-PHASE REMOVAL MECHANISMS

The goal of treating SO_2 and NO contaminated gas streams is their conversion to H_2SO_4 and HNO_3 since these compounds are more easily removed from the gas stream. Gas-phase oxidation of SO_2 by OH produces HSO_3 and H_2SO_4 as shown in Reactions (1) and (2).[16,17] (The reaction

rate constants denoted by k listed below are evaluated at 25°C. They have units $cm^3\ s^{-1}$ unless otherwise noted.)

$$OH + SO_2 \rightarrow HSO_3, \qquad k = 1.1 \times 10^{-12} \tag{1}$$

$$OH + HSO_3 \rightarrow H_2SO_4, \qquad k = 1.0 \times 10^{-11} \tag{2}$$

$O(^3P)$ generated in a plasma can also oxidize SO_2 to form SO_3.[16]

$$O(^3P) + SO_2 \rightarrow SO_3, \qquad k = 5.7 \times 10^{-14} \tag{3}$$

SO_3 is hygroscopic and can be hydrolyzed to form H_2SO_4 if H_2O is available.[16]

$$SO_3 + H_2O \rightarrow H_2SO_4, \qquad k = 9.1 \times 10^{-13} \tag{4}$$

NO can rapidly react with O_3 and is a more efficient free radical scavenger than SO_2. The reactions believed to process NO are presented below.[18-20]

$$NO + O_3 \rightarrow NO_2 + O_2, \qquad k = 1.8 \times 10^{-14} \tag{5}$$

$$NO + OH \rightarrow HNO_2, \qquad k = 6.6 \times 10^{-12} \tag{6}$$

$$NO + HO_2 \rightarrow NO_2 + OH, \qquad k = 8.8 \times 10^{-12} \tag{7}$$

$$NO + N \rightarrow N_2 + O, \qquad k = 2.2 \times 10^{-11} \tag{8}$$

NO_2, is also oxidized by OH radicals to form the desired product HNO_3.[19]

$$NO_2 + OH \rightarrow HNO_3, \qquad k = 1.1 \times 10^{-11} \tag{9}$$

NO_2 can also be oxidized to NO_3 by O_3. NO_3 can then react with NO_2 to form N_2O_5. N_2O_5 can then be hydrolyzed to form HNO_3.[21]

$$NO_2 + O_3 \rightarrow NO_3 + O_2, \qquad k = 3 \times 10^{-17} \tag{10}$$

$$NO_2 + NO_3 \rightarrow N_2O_5, \qquad k = 3 \times 10^{-12} \tag{11}$$

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3, \qquad k = 5 \times 10^{-21} \tag{12}$$

Based on this discussion of reactions of SO_2 and NO, to form H_2SO_4 and HNO_3, and in the context of industrial treatment of large volumetric flow rates, it is essential that gas-phase radicals, such as OH, HO_2, and O, be generated efficiently. There are many plasma-based radical generation techniques, but it is not clear that they are either efficient or scalable.

3. DIELECTRIC BARRIER DISCHARGE PROCESS

DBDs have been widely used as O_3 generators with industrially acceptable efficiencies.[22] In DBDs a dielectric material is placed on one of the two discharge electrodes.[23] Typically, the insulating material has a high

dielectric strength and a high dielectric constant (e.g., glass or ceramic). When the electrical potential across the discharge gap reaches the breakdown voltage, the dielectric acts as a stabilizing material leading to the formation of a large array of microdischarges of short pulses which are distributed spatially and temporally over the discharge gap.[23] Typical duration of these microdischarges is of the order of nanoseconds to some hundreds of nanoseconds depending on the gas composition and discharge configuration.[15] The typical electron temperatures in the microdischarges are a few to 10 eV. These plasmas are ideal for generation of gas-phase radicals in atmospheric-pressure systems.

DBDs have been studied by other researchers to remove SO_2[24-26] and organic compounds such as benzene (C_6H_6) and trichloroethylene (C_2HCl_3)[27-29] from gas streams. Sardja and Dhali[25] reported values of η_{SO_2} of about 50% with an applied voltage of 24 kV ac (peak to peak) and an inlet SO_2 concentration ($[SO_2]$) between 1000 and 5000 ppmv in a dry gas stream containing N_2 and O_2. They proposed that oxidation of SO_2 occurred by reaction with O radical to form SO_3. Research with e-beams indicated that in a dry gas stream, the resulting SO_3 would react with O radical to form SO_2 and O_2.[12] Sardja and Dhali's[25] results thereby imply either total utilization of any O radicals by SO_2 or rapid surface or gas-phase recombination of the O atoms. Experimental results obtained at room temperature by Chang *et al.*[26] are consistent with results by Tokunaga *et al.*,[12] indicating that $H_2O_{(g)}$ is necessary for SO_2 removal with plasmas.

4. EXPERIMENTAL DESIGN

The experimental apparatus consists of a continuous-flow gas generation system, laboratory-scale DBD reactor, and gas detection system (Fig. 1). The system was described in detail by Chang *et al.*,[30] but is briefly described for clarity.

Gas streams containing N_2, O_2, and CO_2 were initially heated to about 350°C to ensure complete evaporation of $H_2O_{(l)}$ droplets that were injected into the gas stream with a peristaltic pump downstream of the heater. $[H_2O_{(g)}]$ of the gas stream was controlled by regulating the volume feed rate of $H_2O_{(l)}$ injected into the gas stream. SO_2 and NO were then added to generate gas streams with known gas compositions, temperatures, and mass flow rates. These gas streams simulated the composition and temperature of gases that result from the combustion of fossil fuels. The gas stream was maintained at atmospheric pressure for all tests.

The DBD reactor was made of a quartz tube with 4 cm inner diameter and 0.2 cm wall thickness. The reactor's inside diameter of 4 cm is large

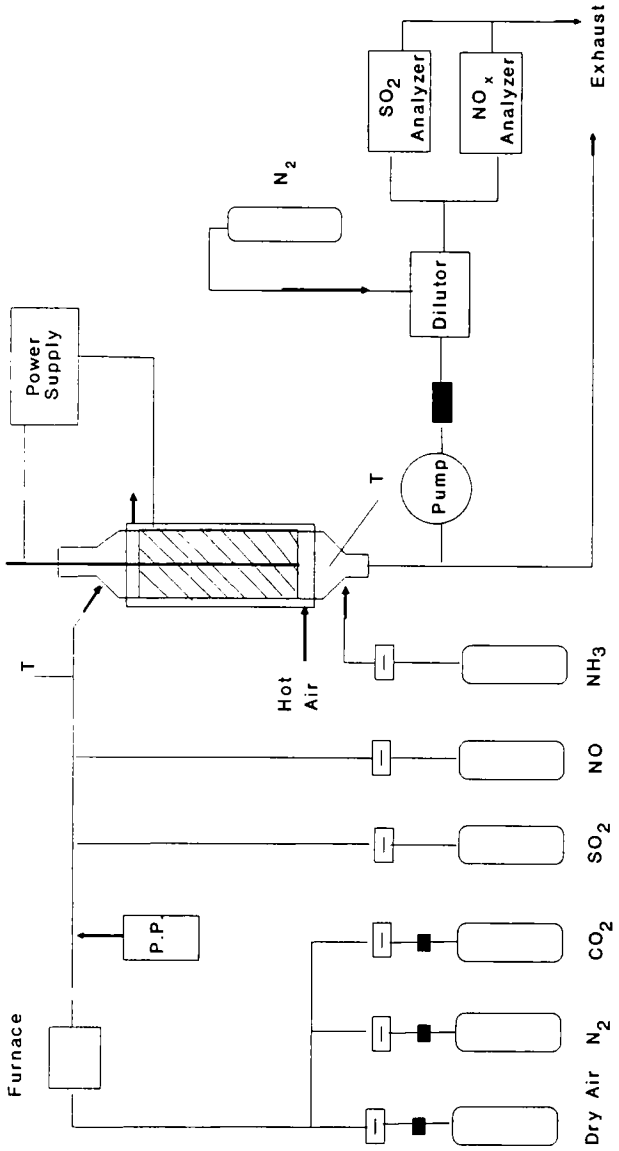

Fig. 1. Schematic of the gas generation system, dielectric barrier reactor, and gas sampling and detection system.

compared to the inside diameters used in DBD reactors for O_3 generation. The larger gap spacing was used to minimize the pressure drop across the cell at high gas flow rates, as would be necessary in industrial applications of this process. One of the coaxial electrodes was made of a 0.24-cm-diameter tungsten rod and the other was stainless steel wire mesh. The rod and wire mesh electrodes were located vertically along the centerline and wrapped around the outside of the reactor, respectively. A 4-mm-diameter glass ball covered the end of the inner electrode to inhibit formation of corona. Near isothermal conditions (±5°C) within the reactor were achieved by forcing countercurrent hot air through a concentric quartz tube surrounding the DBD reactor. The plasma volume was about 350 cm^3. The discharge was sustained by a variable voltage transformer operating at 60 Hz. Depending on the temperature and composition of the gas stream, visible discharges were generally observed with voltage settings larger than 21 kV ac (peak value).

$[SO_2]$ and [NO] were monitored with a fluorescence-detection analyzer and a chemiluminescence-detection analyzer, respectively, after dilution with dry-grade N_2. Dilution was necessary to cool and reduce $[H_2O_{(g)}]$, $[SO_2]$, and [NO] in the gas stream before detection. Prior to the experiments, each analyzer was calibrated with gas streams containing known mixtures of SO_2 and NO to ensure that interferences with the detection of SO_2 and NO did not occur when both gases co-existed in the gas stream.

The NO_x detector (Monitor Lab. Model 8840) is a gas-phase technique that detects the chemiluminescence of activated NO_2 species (NO_2^*) that are generated by the reaction of NO with O_3. The device is able to determine concentrations of NO and NO_x (the sum of [NO] and $[NO_2]$ assuming the lack of any significant interferences) by selectively treating the sample stream with O_3 or with a catalytic converter and O_3. The catalytic converter is used to chemically reduce NO_x to NO before NO reacts with O_3. Evaluation of the chemiluminescence detection of NO and NO_x has indicated that other oxides of nitrogen (besides NO and NO_2) are detected by the NO_x analyzer.[31] All tests performed with the DBD reactor included measurements of NO_x and NO as discussed in Section 5. A more general detector for NO_x in the gas stream, such as a gas chromatograph-mass spectrometer, was not available for these experiments.

Initial conditions were recorded after the system reached steady-state conditions with no power applied to the reactor. Voltage from the power supply was then increased up to 25 kV (peak value) to generate DBDs. $[SO_2]$ and [NO] were then recorded when their new values stabilized. The power supply was then shut off and the system was monitored to ensure that the system returned to its initial condition. η_{SO_2} and η_{NO} were then determined by the difference between their initial concentrations and their

stabilized concentrations divided by their initial concentrations. For instance, η_{NO} was determined by

$$\eta_{NO}(\%) = \left(\frac{[NO_{off}] - [NO_{on}]}{[NO_{off}]}\right)(100\%) \tag{13}$$

where the subscripts denote if the power supply for the DBDs was on or off.

5. RESULTS AND DISCUSSION

The dependences of η_{SO_2} on $[H_2O_{(g)}]$ of the gas stream at 100, 130, and 160°C were initially investigated at 25 kV (peak value) (Fig. 2). The gas flow rate was 2.7 slpm which corresponds to a gas residence time of 5.3 s in the discharge volume for a gas stream at 130°C and 1 atm. Inlet $[SO_2]$ was 1000 ppmv, $[CO_2]$ and $[O_2]$ were 12 and 6% by volume, respectively, and N_2 was the carrier gas. These conditions are typical for gas streams passing through air pollution control devices used downstream of fossil fuel combustors. For dry conditions ($[H_2O_{(g)}] \leq 3$ ppmv), η_{SO_2} was low ($\leq 7\%$) due to the lack of OH radicals.[26] These operating conditions were chosen to determine how $[H_2O_{(g)}]$ would affect η_{SO_2} and to compare our results with those reported by Sardja and Dhali.[25] As $[H_2O_{(g)}]$ increased from 0 to 15% by volume, η_{SO_2} increases monotonically from 7 to 36% at

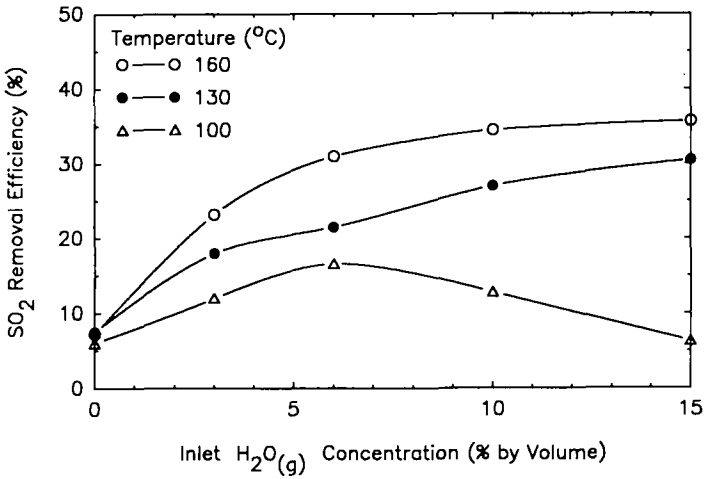

Fig. 2. Dependence of η_{SO_2} on inlet $[H_2O_{(g)}]$ at specified dry-bulb temperatures and 25 kV. Gas streams contain $SO_2/O_2/CO_2 = 0.1\%/6\%/12\%$ by volume, and N_2 as the carrier gas. Increasing $[H_2O_{(g)}] > 6\%$ by volume can either increase or decrease η_{SO_2} depending on the minimum required E/N value.

160°C. η_{SO_2} changes in the same manner at 130°C, whereas at 100°C, η_{SO_2} reaches a local maximum value at 6% by volume $H_2O_{(g)}$ and then decreases with increasing $[H_2O_{(g)}]$. As $[H_2O_{(g)}]$ increases, the generation of OH radicals becomes more efficient and results in higher values for η_{SO_2}. The more efficient production of OH results primarily from direct electron impact on $H_2O_{(g)}$, and H abstraction by $O(^1D)$ from $H_2O_{(g)}$. On the other hand, the gas density N increases as gas temperature decreases. An increase in N results in a lower reduced electric field (E/N) at a constant applied voltage. In addition, $H_2O_{(g)}$ is an electronegative gas which increases the rate of electron attachment, resulting in an increase in the minimum E/N, $(E/N)_0$, required to initiate and sustain the plasma.[30] As $(E/N)_0$ increases, the fraction of the ac cycle over which the plasma can be sustained decreases. Therefore, the decrease in η_{SO_2} at 100°C with increasing $[H_2O_{(g)}] > 6\%$ by volume is most likely a result of reduced power deposition to the gas stream. We were unable to operate at voltages greater than 25 kV to optimize η_{SO_2} due to limitations of the existing power supply.

The dependence of η_{SO_2} on inlet $[CO_2]$ at 23 and 25 kV is shown in Fig. 3. The gas streams contained the specified amount of CO_2, 1000 ppmv SO_2, 6% by volume $H_2O_{(g)}$, 6% by volume O_2, and N_2 as the carrier gas. The temperature was 130°C. η_{SO_2} decreases with increasing $[CO_2]$ up to 12% by volume. The lower values of η_{SO_2} at higher values of $[CO_2]$ are attributed to the electronegative nature of CO_2 which acts to increase

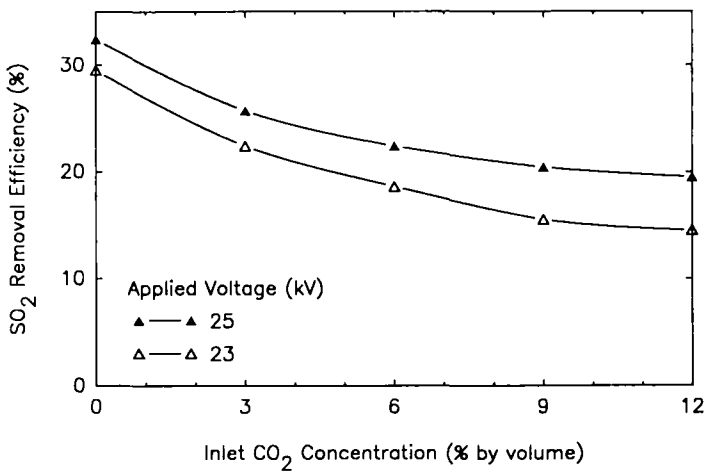

Fig. 3. Dependence of η_{SO_2} on inlet $[CO_2]$ and applied voltage. Gas streams are at 130°C with $SO_2/O_2/H_2O_{(g)} = 0.1\%/6\%/6\%$ by volume, and N_2 as the carrier gas. Decreasing values for η_{SO_2} are likely caused by the electronegative nature of CO_2 which decreases power deposition to the gas stream.

$(E/N)_0$ and hence decreases the power deposited into the gas stream by the plasma. CO_2 can also intercept a significant fraction of the discharge power, producing CO. The resulting CO rapidly reacts with OH, forming H and CO_2. Such reaction reduces the [OH], leaving less OH to chemically react with SO_2.

The rate coefficient for reactions of CO with OH is about 2×10^{-13} cm^3 s^{-1}. If only 1% of the CO_2 that exists at 12% by volume is converted to CO, then the mean reaction time of OH with CO is about 0.2 ms, which is commensurate with the reaction time of OH with a few ppmv of SO_2.

The dependence of η_{SO_2} on inlet [SO_2] ranging from 250 to 1000 ppmv is shown in Fig. 4 for select processing voltages. Although η_{SO_2} is higher at a lower inlet [SO_2], the amount of SO_2 molecules removed from the gas stream is larger for increasing inlet [SO_2]. Therefore, at a constant gas flow rate and power deposited into the gas stream, the rate of SO_2 molecules removed per unit of time also increases with increasing inlet [SO_2]. Note that the absolute removal of SO_2 is a function of specific energy deposited to the gas. Higher total removal can be achieved by operating at higher frequencies. This observation indicates that the reactions are possibly kinetically limited due to the relatively short lifetime of OH radicals reacting with species other than SO_2. This results in a lower absolute removal of SO_2 at a lower inlet [SO_2].[26]

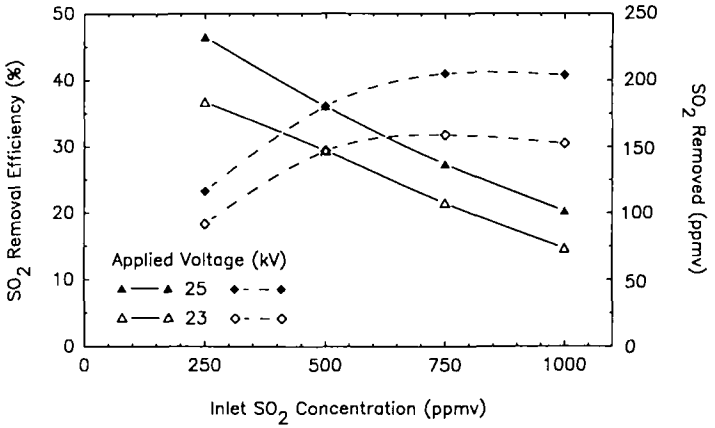

Fig. 4. Percent (solid line) and absolute (dashed line) removal of SO_2 as a function of inlet [SO_2] and voltage at 130°C for gas streams with $O_2/H_2O_{(g)}/CO_2 = 6\%/6\%/12\%$ by volume and N_2 as the carrier gas, at a constant power deposition and increasing inlet concentration of SO_2. The absolute removal of SO_2 increases, while the percent SO_2 removal decreases with increasing inlet [SO_2].

Removal of SO_2 is, to a first order, limited by the rate of generation of OH radicals. If $H_2O_{(g)}$ is not depleted, then the rate of OH generation increases with increasing power deposition, which in turn increases with increasing repetition rate. Since the products of SO_2 removal constitute a small mole fraction, the increase in power deposition should not deplete them by, for example, electron impact dissociation.

Removal of SO_2 ultimately depends on the number of OH radicals produced, which in turn depends to a first order, on power deposition. As $[SO_2]$ increases, this finite supply of OH radicals is used more efficiently. The maximum SO_2 removal will be achieved when $[SO_2]$ is high enough that all OH is consumed by reaction with SO_2. At this point, the absolute value of SO_2 removal can only be increased by a higher rate of generation of OH.

The effect of NH_3 on η_{SO_2} was also evaluated at 130°C (Fig. 5). NH_3 was injected downstream of the reactor to chemically neutralize H_2SO_4 in the gas stream. The amount of back mixing of NH_3 into the plasma was nominal. The inlet gas stream consisted of the specified amount of NH_3, $SO_2/O_2/CO_2/H_2O_{(g)} = 0.1\%/6\%/12\%/6\%$ by volume, and N_2 as the carrier gas. The amount of NH_3 injected into the gas stream is expressed as the stoichiometric ratio (SR) which is defined below:

$$SR = \frac{[NH_3]}{2[SO_2]+[NO]} \tag{14}$$

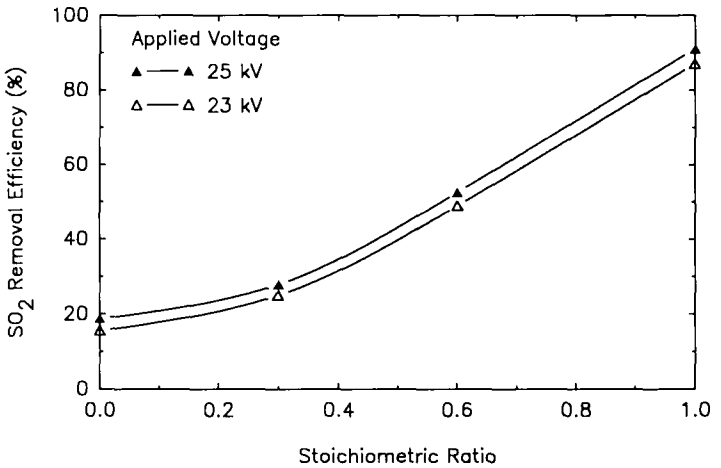

Fig. 5. η_{SO_2} as a function of stoichiometric ratio at 130°C for gas streams containing $SO_2/O_2/H_2O_{(g)}/CO_2 = 0.1\%/6\%/6\%/12\%$ by volume, and N_2 as the carrier gas. Increasing values for η_{SO_2} with increasing stoichiometric ratio are likely caused by thermal reactions between SO_2 and NH_3.

SR is defined as the ratio of actual moles of NH_3 injected into the gas stream divided by the number of stoichiometric moles of NH_3 needed to chemically neutralize the H_2SO_4 [Eq. (15)] and HNO_3 [Eq. (16)] that would exist in the gas stream if all of the SO_2 is oxidized to H_2SO_4 and all of the NO is oxidized to HNO_3.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 \tag{15}$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{16}$$

η_{SO_2} increases from 20 to 90% as SR increases from 0 to 1. To clarify the effects of NH_3 injection and DBDs on η_{SO_2}, NH_3 was also injected upstream of the reactor and injected without the generation of the DBDs. Experimental results obtained all agree well (within 5%) with that reported in Fig. 5, and white solid particles were observed to deposit on the inner wall of the reactor and tubing during all three cases. These observations indicate that SO_2 removal was mostly attributed to thermal reactions between SO_2, NH_3, and $H_2O_{(g)}$ rather than simple chemical neutralization of H_2SO_4 by NH_3 or other plasma reactions between NH_3 and gas-phase radicals.

The thermal reactions between SO_2, NH_3, and $H_2O_{(g)}$ have been studied by other researchers,[32-36] and in fact NH_3 injection has been proposed as a method to remove SO_2 from flue gas streams.[37] The thermal reactions responsible for SO_2 removal are believed to include at least the following six reactions[33]:

$$NH_3 + SO_2 \rightleftarrows NH_3SO_{2(s)} \tag{17}$$

$$2NH_3 + SO_2 \rightleftarrows (NH_3)_2SO_{2(s)} \tag{18}$$

$$2NH_3 + 2SO_2 + H_2O \rightleftarrows (NH_4)_2S_2O_{5(s)} \tag{19}$$

$$2NH_3 + SO_2 + H_2O \rightleftarrows (NH_4)_2SO_{3(s)} \tag{20}$$

$$2NH_3 + SO_2 + 2H_2O \rightleftarrows (NH_4)_2SO_3H_2O_{(s)} \tag{21}$$

$$NH_3 + SO_2 + H_2O \rightleftarrows NH_4HSO_{3(s)} \tag{22}$$

Although the precise rate coefficients for these processes are not known, experimental results[33] place a lower limit on the effective rate coefficient for SO_2 removal by NH_3 of 10^{-16} cm^3 s^{-1}.

The use of DBDs to simultaneously remove SO_2 and NO from gas streams was evaluated at 100, 130 and 160°C, respectively (Fig. 6). Inlet

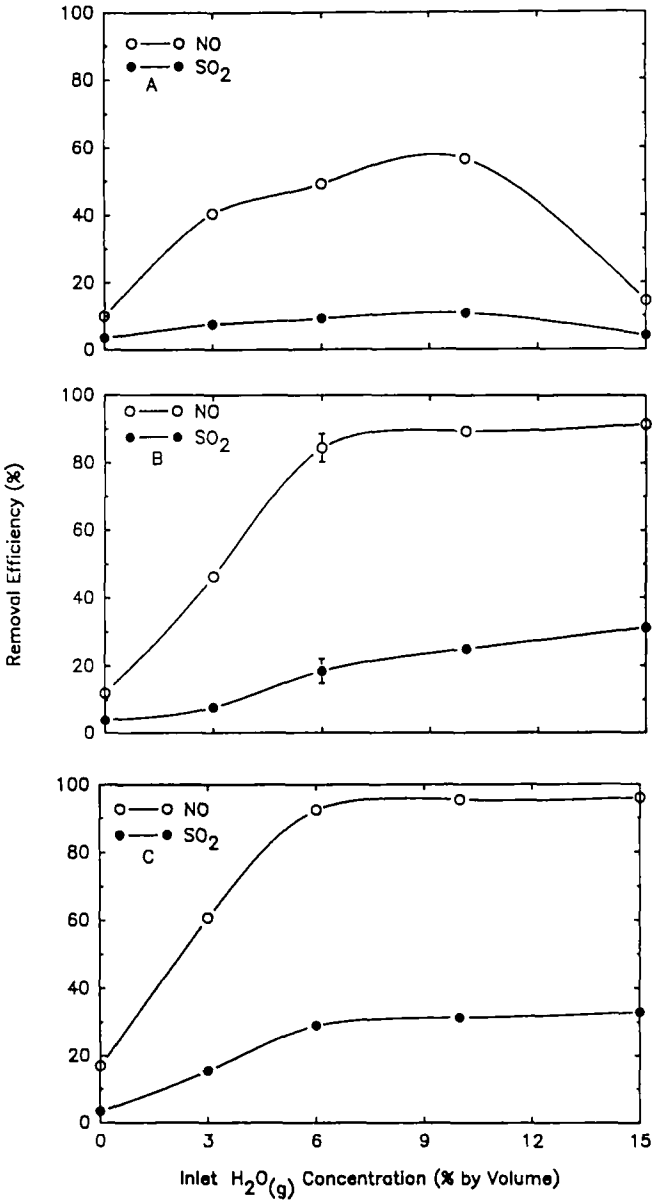

Fig. 6. Dependence of η_{SO_2} and η_{NO} on inlet $[H_2O_{(g)}]$ at 100°C (A), 130°C (B), and 160°C (C) for gas streams containing $SO_2/NO/O_2/CO_2 = 0.1\%/0.25\%/6\%/12\%$ by volume, and N_2 as the carrier gas. The applied voltage is 25 kV.

$[SO_2]$ and [NO] in the gas streams were 1000 and 250 ppmv, respectively. Error bars for η_{SO_2} and η_{NO} represent the standard deviations of the test results obtained from four separate sets of measurements. Other results describing the experimental errors have been reported.[30] η_{SO_2} and η_{NO} increase with increasing temperature, in part, as a result of the increase in E/N. At 130 and 160°C, η_{SO_2} and η_{NO} also increase with increasing $[H_2O_{(g)}]$ due to more efficient generation of OH radicals. At 160°C, with 15% by volume $H_2O_{(g)}$ in the gas stream, more than 95% of the NO and 32% of the SO_2 are simultaneously removed from the gas stream. However, reduced values for η_{SO_2} and η_{NO} were obtained at 100°C with 15% by volume $H_2O_{(g)}$, primarily due to lower power deposition to the gas stream.

Removal of NO_x, which includes NO and NO_2, was also investigated. With O_2 in the gas stream, a portion of NO is oxidized to form NO_2 and is detected as NO_x. Such oxidation results in $[NO_x]$ being about 30 ppmv higher than [NO]. In all tests, η_{NO_x} closely followed the same trends as η_{NO} except η_{NO_x} was about 10% to 15% lower than η_{NO} (e.g., 80% for η_{NO} compared to 65–70% for η_{NO_x}). Lower values for η_{NO_x} compared with η_{NO} are attributed to the slightly higher inlet $[NO_x]$, the possible oxidation of NO to NO_2 instead of to HNO_3, and the possible existence of other oxides of nitrogen that are detectable by chemiluminescence.

The value of η_{SO_2} is lower than that of η_{NO}, under the same operating conditions, due to the higher inlet $[SO_2]$ and lower reaction rate constants for SO_2 and gas-phase radicals as previously described. η_{SO_2} can be increased by operating the DBD reactor at higher power deposition. Nevertheless, simultaneous removal of SO_2 and NO from gas streams can be achieved with DBDs.

The dependence of the simultaneous removal of SO_2 and NO on NH_3 injection was also evaluated (Fig. 7). As SR increases from 0 to 1, η_{SO_2} increases from 10 to 100% while η_{NO} remains nearly constant. η_{SO_2} is higher during these tests compared with tests removing SO_2 only with NH_3 injection because NH_3 that was to react with NO actually reacted with SO_2. Injection of NH_3 did not appear to affect η_{NO} at these relatively low temperatures because NH_3 is unreactive with NO over time scales of 1–10 sec. Increased η_{SO_2} with NH_3 injection is attributed to the previously mentioned thermal reactions between NH_3 and SO_2 instead of chemical reactions associated with the DBD plasma.

Accurate measurement of the power deposited into the gas stream[38] is difficult with the power supply used to generate the DBDs,[30] although results from experimental and numerical modeling estimate that tens of millijoules per milliliter of gas is required to remove 90% of the NO from a gas stream initially containing 250 ppmv of NO.[26]

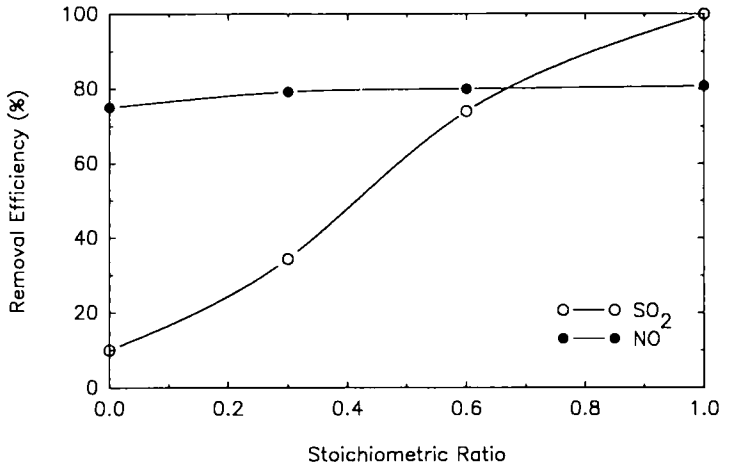

Fig. 7. η_{SO_2} and η_{NO} as a function of stoichiometric ratio at 130°C for gas streams containing $SO_2/NO/O_2/H_2O_{(g)}/CO_2 = 0.1\%/0.025\%/5\%/6\%/12\%$ by volume, and N_2 as the carrier gas. The applied voltage is 25 kV. Increasing values for η_{SO_2} with increasing stoichiometric ratio are likely caused by thermal reactions between SO_2 and NH_3.

6. SUMMARY AND CONCLUSIONS

The effectiveness of using dielectric barrier discharges to remove SO_2 and to simultaneously remove SO_2 and NO from gas streams was evaluated experimentally with a laboratory-scale reactor. Removal efficiencies of SO_2 and NO are dependent on applied voltage, inlet concentrations of SO_2, NO, and $H_2O_{(g)}$, and temperature of the gas stream. Simultaneous removal efficiencies for SO_2 and NO at inlet concentrations of 1000 and 250 ppmv are as high as 32 and 95%, respectively. Higher temperatures result in higher removal efficiencies for a given applied voltage due to higher reduced electric field values. NH_3 injection enhances SO_2 removal to 100% most likely by thermal reactions between SO_2 and NH_3. These results indicate that DBD plasmas have the potential to simultaneously remove SO_2 and NO from gas streams generated by large-scale fossil fuel combustors.

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REFERENCES

1. J. D. Spengler, M. Brauer, and P. Koutrakis, *Environ. Sci. Technol.* **24**, 946 (1990).
2. P. J. Temple, *J. Air Pollut. Control Assoc.* **22**, 271 (1972).
3. E. O. Edney, D. C. Stiles, and J. W. Spence, A Laboratory Study to Evaluate the Impact of NO_x and Oxidants on Atmospheric Corrosion of Galvanized Steel, *ACS Symp. Ser.* 318, 172 (1986).
4. E. B. Cowling, *Environ. Sci. Technol.* **16**, 110A (1982).
5. M. E. Bassett and J. H. Seinfeld, *Atmos. Environ.* **18**, 1163 (1984).
6. C. S. Sloane and G. T. Wolff, *Atmos. Environ.* **19**, 669 (1985).
7. H. B. Singh, *Environ. Sci. Technol.* **21**, 320 (1987).
8. C. V. Mathai, *J. Air Waste Manage. Assoc.* **40**, 1486 (1990).
9. L. M. Thomas, *USEPA J.* (Oct. 1987).
10. S. Jordan, *Radiat. Phys. Chem.* **31**, 21 (1988).
11. S. Machi, O. Tokunaga, K. Nishimura, S. Hashimoto, W. Kawakami, and M. Washino, *Radiat. Phys. Chem.* **9**, 371 (1977).
12. O. Tokunaga, K. Nishimura, and M. Washino, *International Journal of Applied Radiation and Isotopes* **29**, 87 (1978).
13. N. Frank, S. Hirano, and K. Kawamura, *Radiat. Phys. Chem.* **31**, 57 (1988).
14. H. R. Paur, S. Jordan, and W. Baumann, *J. Aerosol Sci.* **19**, 1397-1400 (1988).
15. B. Eliasson and B. Gellert, *J. Appl. Phys.* **68**, 2026 (1990).
16. J. G. Calvert and W. R. Stockwell, *Mechanism and Rates of the Gas-Phase Oxidations of Sulfur Dioxide and Nitrogen Oxides in the Atmosphere*, Ann Arbor Scientific Publication, Ann Arbor (1984).
17. F. Yin, D. Grosjean, and J. H. Seinfeld, *J. Geophy. Res.* **91**, 14417 (1986).
18. J. D. Butler, *Air Pollution Chemistry*, Academic Press, New York (1979), p. 275.
19. D. L. Baulch, R. A. Cox, and P. J. Crutzen, *J. Phys. Chem. Ref. Data* **11**, 327 (1982).
20. O. Tokunaga and N. Suzuki, *Radiat. Phys. Chem.* **24**, 145 (1984).
21. C. Willis and A. D. Boyd, *Int. J. Radiat. Phys. Chem.* **8**, 71 (1976).
22. U. Kogelschatz, B. Eliasson, and M. Hirth, *Ozone Sci. Technol.* **10**, 367 (1988).
23. B. Eliasson, M. Hirth, and U. Kogelschatz, *J. Phys. D: Appl. Phys.* **20**, 1421 (1987).
24. W. R. Browne and E. E. Stone, Sulfur Dioxide Conversion under Corona Discharge Catalysis, prepared for HEW under contract PH 86-65-2 (1965).
25. I. Sardja and S. K. Dhali, *Appl. Phys. Lett.* **56**, 21 (1990).
26. M. B. Chang, J. H. Balbach, M. J. Rood, and M. J. Kushner, *J. Appl. Phys.* **69**, 4409 (1991).
27. W. C. Neely, E. I. Newhouse, and S. Pathirana, *Chem. Phys. Lett.* **155**, 381 (1989).
28. J. W. Bozzelli and R. B. Barat, *Plasma Chem. Plasma Process.* **8**, 293 (1988).
29. G. H. Ramsey, N. Plaks, W. H. Ponder, B. E. Daniel, and L. E. Hamel, Proceedings of the 83rd Annual Air and Waste Management Association Meeting, Pittsburgh, Pennsylvania, Paper No. 90-109.2 (1990).
30. M. B. Chang, M. J. Kushner, and M. J. Rood, *Environ. Sci. Technol.* **26**, 777-781 (1992).
31. A. M. Winer, J. W. Peters, J. P. Smith, and J. N. Pitts, Jr., *Atmos. Environ.* **18**, 5 (1984).
32. J. C. Person and D. O. Ham, *Radiat. Phys. Chem.* **31**, 1 (1988).

33. H. Bai, P. Biswas, and T. C. Keener, Proceedings of the 84th Annual Air and Waste Management Association Meeting, Vancouver, B.C., Canada, Paper No. 91-103.24 (1991).
34. R. Landreth, R. G. de Pena, and J. Heicklen, *J. Phys. Chem.* **89**, 9 (1985).
35. R. W. Tock, K. C. Hoover, and G. J. Faust, SO_2 Removal by Transformation to Solid Crystals of NH_3 Complexes, *AIChE Symp. Ser.* 188, 75 (1979).
36. T. C. Keener and W. T. Davis, Demonstration of a $Ca(OH)_2/NH_3$ Based System for the Removal of SO_2 on High Sulfur Coals, Ohio Coal Development Office, Columbus, Ohio, August, 1988.
37. C. C. Shale, Ammonia Injection: A Route to Clean Stacks, *Pollution Control and Energy Needs*, R. M. Jimeson and R. S. Spindt, eds., Advances in Chemistry Series, **127**, 195-205 (1973).
38. J. J. Carlins, *Environ. Prog.* **1**, 2, 113-118 (1982).