Gas-phase Removal of SO_2 and NO with Dielectric Barrier Discharges

以介電質放電法去除SO_2及NO之可行性研究

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摘 要

大眾對酸性沉降之關切已導致世界各國對SO_2及NO之排放，採取更嚴格之標準。鑑於目前各種控制方法之限制，有必要研究更有效之控制技術以因應未來之需要。本研究旨在探討利用介電質放電法以同時自氣流中去除SO_2及NO之可行性。其過程是藉介電質放電產生OH、HO_2及O等自由基利用氣態氧化原理將氣體中之SO_2及NO氧化成硫酸與硝酸再移除之，亦可加入NH_3中和後再去除。實驗結果顯示，氣流之溫度爲160℃時，SO_2之去除效率爲35％，而NO之去除效率可達99％，此去除效率受使用電壓，氣流成份及溫度、氣體停留時間等操作參數之影響。此研究顯示，未來以介電質放電法同時去除氣流之SO_2及NO甚具潛力。

關鍵詞：氣態氧化，二氧化硫去除，氮氧化物去除，介電質放電

ABSTRACT

Concern over acid deposition has reulted in more stringent SO_2 and NO_x emission standards as designated by the 1990 Clean Air Act Amendments. In view of the more stringent

emission standards and the constraints of current air pollution control technology for removing SO_2 and NO from gas streams, more effective air pollution control technologies should be searched. An innovative gas phase oxidation method using dielectric barrier discharges (DBDs) has been developed to simultaneously remove SO_2 and NO from gas streams. This process generates gas phase radicals such as OH, HO_2, and O. The radicals can then oxidize gaseous SO_2 and NO to form particles consisting of H_2SO_4 and HNO_3, respectively. The resulting compounds can then be chemically neutralized with NH_3 and removed from the gas stream by othe conventional air pollution control devices. The effectiveness of DBDs to remove SO_2 and NO from gas streams has been evaluated with a laboratory- scale reactor. Experimental results showed that about 35 % of SO_2 can be removed from the gas stream at 160 ℃ with DBDs. This removal efficiency was achieved for a gas stream with an inlet SO_2 concentration of 1000 ppmv, H_2O concentration of 15 % by volume, CO_2 concentration of 12 % by volume, O_2 concentration of 6 % by volume with N_2 as the carrier gas. The gas residence time is 5 sec and processing voltage is 25 kv (peak value). 99 % removal efficiency for NO was also achieved for the gas stream with an inlet NO concentration of 250 ppmv at the same operating conditions described above. These results indicated that DBDs have the potential to simultaneously remove SO_2 and NO from gas streams generated by large scale sources of SO_2 and NO, such as a coal-fired power plant.

Key words: Gas-phase oxidation, SO_2 removal, NO removal, dielectric barrier discharges

INTRODUCTION

SO_2 and NO_x (includes NO and NO_2) have been designated as gaseous air contaminants for decades due to their adverse effects on human health (Spengler *et al.* 1990), damage to vegetation (Temple 1972), and degradtion of materials (Edney *et al.* 1986). SO_2 and NO are also the two most important precursors leading to acid deposition. In addition, SO_2 and NO contribute to the degradation of visibility since they form accumulation mode aerosol particles (diameter < 2 μ m) containing sulfates and nitrates via gas-to-particle conversion (Basett and Seinfeld 1984; Slone and Wolff 1985). Furthermore. NO chemically reacts with gaseous hydrocarbons in the atmosphere to form noxious photochemical contaminants such as ozone (O_3) and peroxyacetal nitrate (PAN) (Singh 1987). In recent years, degradation of visibility at some national parks in the United States and the widespread failure to attain the National Ambient Air Quality Standards for O_3 in large metropolitan areas such as Los Angeles and Chicago have caused public concern (Mathai 1990; Thomas 1987).

Exhaust gases from the combustion of coal and oil are major manmade sources of SO_2

and NO. During 1985, approximately 21 x 10^6 tons of SO_2 and 19 x 10^6 tons of NO_x (as NO and NO_2) were released into the atmosphere by anthropogenic sources in the United States (NAPAP 1990). Concern over the adverse effects of SO_2 and NOx on human health, vegetation , materials, visibility, and acid deposition has resulted in more stringent emission standards of SO_2 and NO_x into the atmosphere as designated in the Clean Air Act Amendments of 1990 (PL 101-549, 1990). These amendments require reductions in the amount of emissions of SO_2 and NO_x by 10 x 10^6 and 2 x 10^6 tons/yr, respectively.

The primary anthropogenic source of SO_2 is combustion of fossil fuels that contain sulfur. Reduction of SO_2 emission can be achieved through fuel substitution or the use of flue gas desulfurization (FGD) tenchnology. Wet scrubbing process, spray-drying and duct injection technologies have been widely applied to achieve FGD in industry.

Utilities and other combustion processes contribute more than 55 % of NO_x emission in the U.S. (NAPAP 1990). About 90-95 % of NO_x emitted from combustion sources exists as NO but forms other oxides of nitrogen in the atmosphere. As a result, reducing the amounts of NO emitted from large point sources would reduce the NO_x concentration in the atmosphere, and therefore reduce its adverse effects. Abatement of NO_x emission can be achieved by 1) combustion control methods, such as applying low NO_x burners, gas recirculation, and staged combustion, and 2) flue gas treatment (FGT) technology. Selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) processes have been developed for industry to remove NO_x from gas streams.

As the emission standards for SO_2 and NO_x get more stringent, the cost to control these contaminants also escalates. In view of the more stringent emission standards of the 1990 Clean Air Act Amendments and the constraints of current technology for removing SO_2 and NO from gas streams, it would be more cost-effective to simultaneously remove SO_2 and NO from gas streams in a single process. Gas phase oxidation process using electron beam (e-beam) technology has been demonstrated to simultaneously remove SO_2 and NO from a gas stream without creating sludge handling problems (Jordan 1988). Removal efficiencies for SO_2 and NO are over 90 % and 80 %, respectively, with e-beam technology (Frank *et al.* 1988). Nevertheless, high cost and potential x-ray hazard of the process have motivated research into more effective gas phase oxidation processes.

This paper discussed an innovative gas phase oxidation process that simultaneously removes SO_2 and NO from gas streams. The process used dielectric barrier discharges (DBDs) to generate gas phase radicals, such as hydroxyl (OH) and hydroperoxyl (HO_2), that simultaneously oxidize SO_2 and NO to form particles consisting of H_2SO_4 and HNO_3, respectively (Chang *et al.* 1991; Chang *et al.* 1992). The resulting compounds can then be chemically neutralized with NH_3 to form ammonium particles such as $(NH_4)_2SO_4$ and NH_4NO_3 which can

then be removed from the gas stream by a particle removal device, such as a fabric filter or electrostatic precipitator (ESP) (Paur *et al.* 1988). DBD was chosen for this study for its relatively low cost and high efficiency in generating gas phase radicals (Eliasson and Gellert 1990).

GAS-PHASE REMOVAL MECHANISMS

1. SO_2 Removal Mechanisms

Gas phase oxidation of SO_2 is primarily accomplished by OH radicals as shown in Reactions (1) and (2) (Calvert and Stockwell 1984; Yin *et al.* 1986).

Reaction Mechanism	k(cm^3/molecule-s)	
$OH + SO_2 \longrightarrow HSO_3$	1.1×10^{-12}	(1)
$OH + HSO_3 \longrightarrow H2SO_4$	1.1×10^{-11}	(2)

Besides, $O(^3P)$ generated in a plasma can also oxidize SO_2 to form SO_3 as shown in Reaction (3) (Calvert and Stockwell, 1984).

Reaction Mechanism	k(cm^3/molecule-s)	
$O(^3P) + SO_2 \longrightarrow SO_3$	5.7×10^{-14}	(3)

SO_3, the product of Reaction (3), is highly hygroscopic and can then be hydrolyzed to form H_2SO_4 if H_2O is available as presented in Reaction (4) (Calvert and Stockwell 1984).

Reaction Mechanism	k(cm^3/molecule-s)	
$SO_3 + H_2O \longrightarrow H_2SO_4$	9.1×10^{-13}	(4)

The reaction rate constants listed for Reactions (1) through (4) are evaluated at 25℃

2. NO Removal Mechanisms

No is a more efficient free radical scavenger than SO_2, hence, it can react more rapidly with OH, HO_2, O_3, and N, as demonstrated in the following reactions and reaction rate constants at 25℃ (Butler 1979; Baulch *et al.* 1982; Tokunaga and Suzuki 1984).

Reaction Mechanism	k(cm^3/molecule-s)	
$NO + OH \longrightarrow HNO_2$	6.6×10^{-12}	(5)
$NO + HO_2 \longrightarrow NO_2 + OH$	8.8×10^{-12}	(6)
$NO + O_3 \longrightarrow NO_2 + O_2$	1.8×10^{-12}	(7)
$NO + N \longrightarrow N_2 + O$	2.2×10^{-11}	(8)

NO_2, the product of Reactions (6) and (7), is than oxidized by the OH radical to form HNO_3 via Reaction (9) (Baulch *et al.* 1982).

Reaction Mechanism	k(cm^3/molecule-s)

$NO_2 + OH \longrightarrow HNO_3$ 1.1×10^{-11} (9)

If O_3 exists in the gas stream, NO_2 can also be oxidized to NO_3 which can then react with NO_2 to form N_2O_5 can then be hydrolyzed to form N_2O_5. N_2O_5 can then be hydrolyzed to form HNO_3 as shown in Reactions (10) through (12) (Willis and Boyd 1976).

Reaction Mechanism	k(cm^3/molecule-s)	
$NO_2 + O_3 \longrightarrow O_3 + O_2$	8×10^{-17}	(10)
$NO_2 + NO_3 \longrightarrow N_2O_5$	3×10^{-12}	(11)
$N_2O_5 + H_2O \longrightarrow 2HNO_3$	5×10^{-21}	(12)

Based on the previous discussion of reactions of SO_2, No, and gas phase radicals, it is essential that gas phase radicals, such as OH, HO_2 and O, be efficiently generated for gas phase oxidation to occur. These gas phase radicals can then chemically react with SO_2 and NO to form H_2SO_4 and HNO_3, respectively.

DIELECTRIC BARRIER DISCHARGE PROCESS

DBD, also known as silent discharge, is a gas discharge process which has been widely used for large-scale O_3 generation (Kogelschatz *et al.* 1988). The main characteristic of DBD is the presence of a dielectric material between the discharge gap and one of the two discharge electrodes (Eliasson *et al.* 1987). Typically, a material with high dielectric strength (V/mm) and a high dielectric constant, such as glass or ceramics, is used as the dielectric. When the potential across the gap reaches breakdown voltage, the dielectric acts as a stabilizing material leading to the formation of a large number of microdischarges of short pulses which are statistically spread spatially and temporally over the discharge gap (Eliasson *et al.* 1987). Typical duration of these microdischarges is of the order of nanoseconds to some hundreds of nanoseconds depending on the gas composition and discharge configuration (Eliasson and Gellert 1990).

Due to the large electric field strength in these microdischarges, existing electrons are accelerated to reach average energies in the range 1-20 eV (Eliasson and Gellert 1990). Electrons with this level of energy can cause excitation, ionization, and dissociation of gas molecules, resulting in the formation of gas phase radicals. Generation of OH, HO_2, O_3, and O by DBDs depends on (1) the magnitude of voltage and frequency of power supply, (2) configuration of the reactor, and (3) gas stream composition, pressure, and temperature (Kogelschatz *et al.* 1988). DBDs have been studied by other researchers to remove SO_2 (Browne and Stone 1965: Sardja and Dhali 1990; Chang *et al.* 1991) and organic compounds such as benzene (C_6H_6) and trichloroethylene (C_2HCl_3) (Neely *et al.* 1989; Bozzeli and Barat 1988, ; Ramsey *et al.* 1990) from gas streams.

EXPERIMENTAL DESIGN

An experimental apparatus has been constructed (Figure 1) to evaluate the effectiveness of applying DBDs to remove SO_2 and NO from gas streams. The experimental apparatus was comprised of a continuous flow gas generation system, laboratory-scale DBD reactor, and gas detection system. The gas generation system consists of an electrical heater and compressed gas sources which are regulated by mass flow controllers. The gas stream containing N_2, O_2 and CO_2 was initially heated to ~ 350 ℃ to ensure complete evaporation of tiny $H_2O_{(l)}$ droplets that would be injected into the gas stream with a peristaltic pump. The resulting [$H_2O_{(g)}$] of the gas stream was controlled by regulating the volume feed rate of $H_2O_{(l)}$ injected into the high-temperature gas stream. SO_2 and NO were then added to generate gas streams with specific gas composition and mass flow rates. The gas stream was maintained at atmospheric pressure in the DBD reactor for all tests.

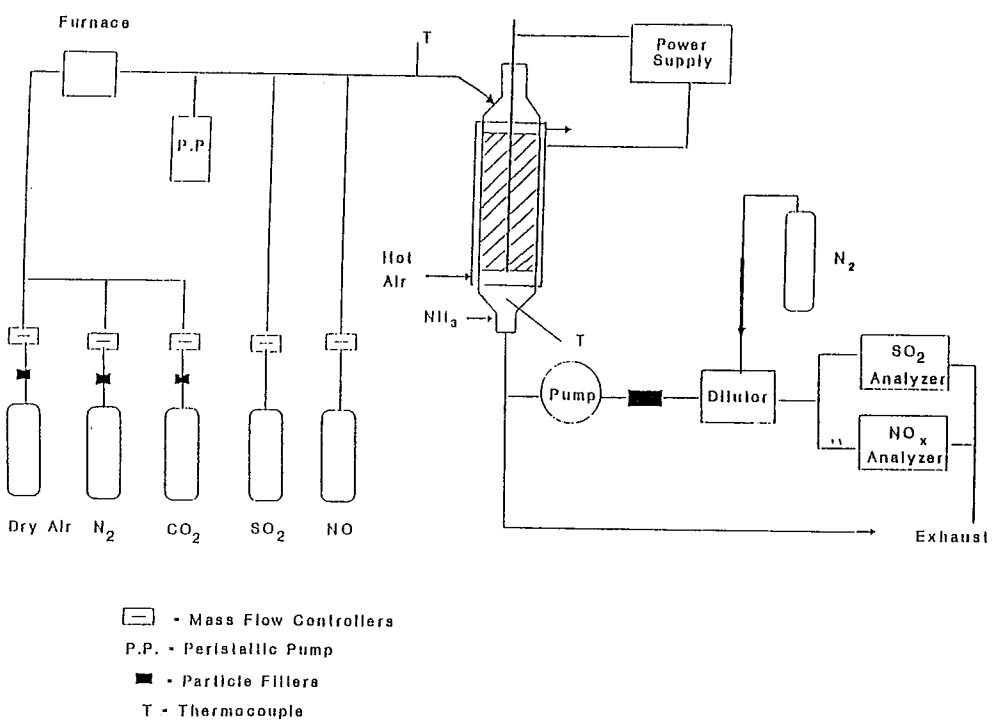


Figure 1. Schematic of the gas generation system, dielectric barrier reactor, and gas sampling and detection system.

The DBD reactor was made of a quartz tube with 4 cm inner diameter and 0.2 cm wall thickness. One of the coaxial electrodes was made of a 0.24 cm diameter tungsten rod and the other with 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 glass ball with 4 mm diameter covered the end of the inner electrode to inhibit localized electrical discharges. Near isothermal conditions (± 5 ℃) within the reactor was achieved by forcing hot air to flow through the air jacket. The plasma volume is about 350cm^3 which is 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 (peak value).

[SO_2] and [NO] were monitored with a fluorescence-detection analyzer (Monitor Laboratory Inc., Model 8730 HL) and a chemiluminescence-detection analyzer (Monitor Laboratory Inc., Model 8840 HL), respectively, after dilution with dry-grade N_2 by a dilution pump. Dilution was necessary to cool and reduce the [$H_2O_{(g)}$] , [SO_2] and [NO] in the gas stream before detection, and therefore to protect the SO_2 and NO analyzers.

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 DBD. The [SO_2] and [NO] were then recorded when their new values became stabilized. Thereafter, the power supply was shut-off and the system was monitored to ensure that the system returned to its initial conditions. The removal efficiency (η) was then determined by the ratio of the difference between the initial concentration the stabilized concentration to the initial concentration. For instance, the percent of NO removed from the gas stream, η_{NO}, was determined by Equation (A).

$$\eta_{NO}(\%) = \frac{[NO_{off}] - [NO_{on}]}{[NO_{off}]} \times 100\%$$

where the subscripts denote flowing operation of the cell with the DBDs on and off, respectively.

RESULTS AND DISCUSSION

Experimental tests were first completed to describe the dependencies of η SO_2 on [$H_2O_{(g)}$] of the gas stream and processing voltage at 160 ℃ . The processing voltage varied from 21 KV to 25 kV (peak value) (Figure 2). The gas flow rate was controlled at 2.7 slpm which corresponds to a gas residence time of 5.0 seconds in the discharge volume for a gas stream of 160 ℃ and 1 atm. The inlet [SO_2] was kept at 1000 ppmv while [CO_2] and [O_2] at

12 % and 6 % by volume. respectively, with N_2 as the carrier gas. Under dry conditions ($[H_2O_{(g)}]$ <= 3 ppmv. RH ~ 0 %), η SO_2 was low (<= 7 %) due to the lack of OH radicals (Chang *et al.* 1991). As $[H_2O(g)]$ increases from 0 % to 15 % by volume. η SO_2 increases monotonically from 7 % to 36 % with processing voltage of 25 KV. η SO_2 changes in the same manner with 23 KV, whereas, η SO_2 reaches the local maximum at 6 % by voiume $[H_2O_{2(g)}]$ and then decreases with increasing $[H_2O_{(g)}]$ when the processing voltage was kept at 21 KV. As $[H_2O_{(g)}]$ increases, the generation of OH radicals becomes more efficient and results in a higher nSO_2 as long as the processing voltage is high enough to sustain the plasma. The more efficient production of OH results primarily from direct electron impact on $H_2O_{(g)}$, and H abstraction by $O(^1D)$ from $H_2O_{(g)}$ (Chang *et al.* 1991). However, $H_2O_{(g)}$ is an electronegative gas which increases the rate of electron attachment, resulting in increasing the minimum E/N, $(E/N)_0$, required to initiate and sustain the plasma (Chang *et al.* 1992), therefore, decreases η_{SO2} due to lower power deposition at low processing voltage (21 KV).

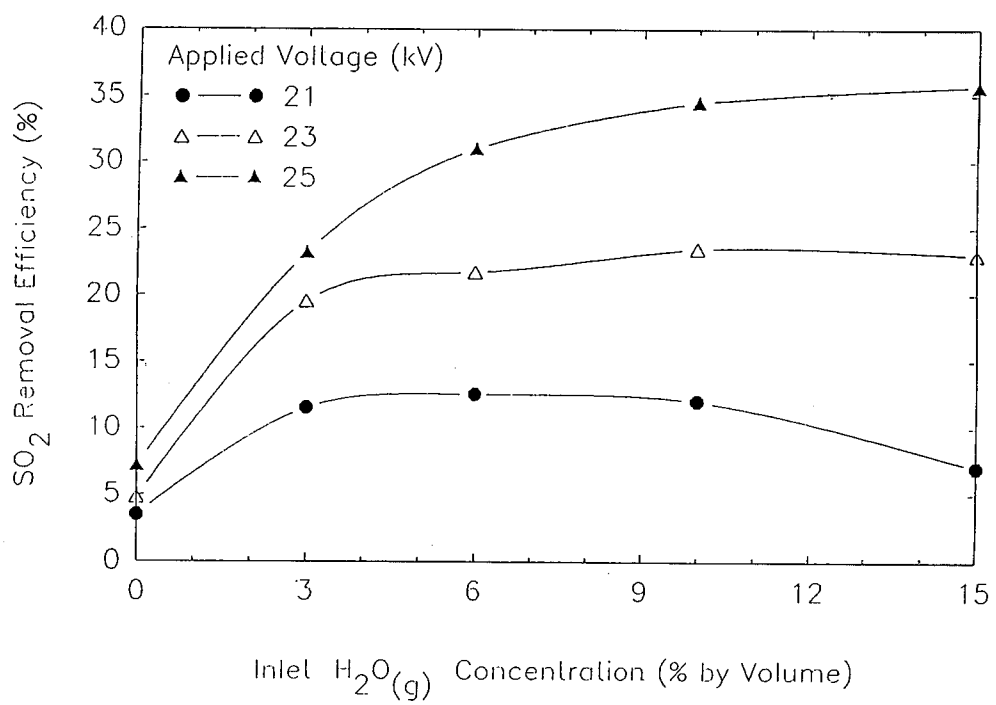


Figure 2. Dependence of η_{so2} on inlet [$H_2O_{(g)}$] at specified processing voltage and at 160 ℃ for gas streams containing 1000 ppmv SO_2, 6% by volume O_2, 12% by volume CO_2, and N_2 as the carrier gas.

Dependence of η_{NO} on $[H_2O_{(g)}]$ of the gas stream and processing voltage achieved by DBDs at 160 ℃ was also experimentally determined (Figure 3). The inlet [NO] of the gas stream was controlled at 250 ppmv while $[CO_2]$ and $[O_2]$ at 12 % and 6 % by volume, respectively, with N_2 as the carrier gas. With constant $[H_2O_{(g)}]$ of the gas stream, a higher processing voltage provides a higher power input leading to higher nNO. A higher n_{NO} was obtained at a higher $[H_2O_{(g)}]$ of the gas stream due to more efficient generation of OH and HO_2 radicals. With 15 % of $[H_2O_{(g)}]$ in the gas stream, 99 % of NO was removed from the gas stream when the processing voltage was kept at 25 KV.

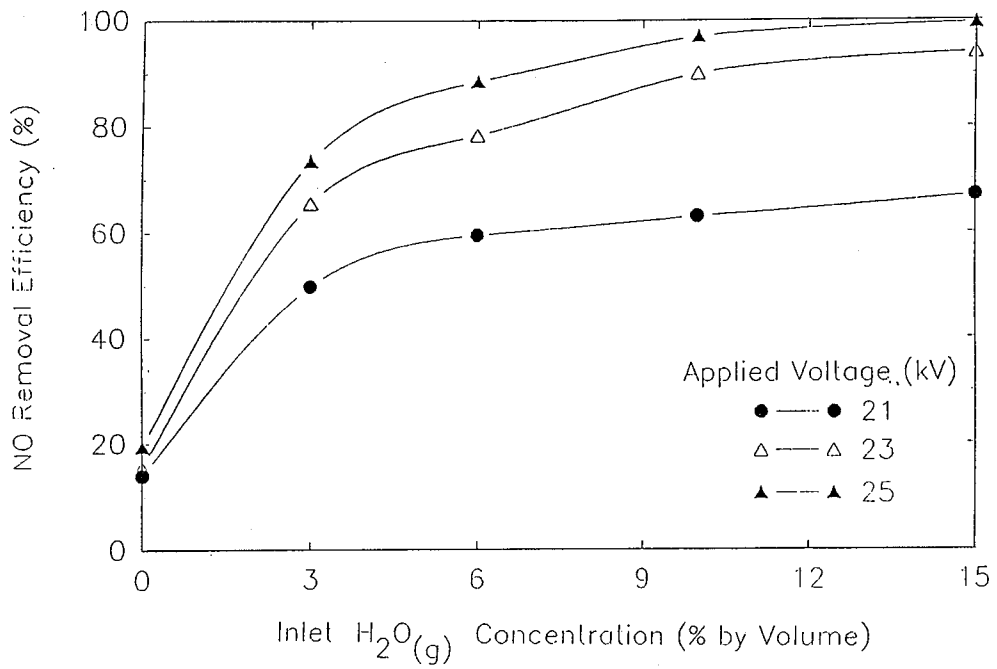


Figure 3. Dependence of η_{No} on inlet $[H_2O_{(g)}]$ at specified processing voltage and at 160℃ for gas streams containing 250 ppmv NO, 6% by volume O_2, 12% by volume CO_2, and N_2 as the carrier gas.

The potential of applying DBDs to simultaneously remove SO_2 and NO from gas streams was also experimentally evaluated at 160 ℃ as shown in Figure 4. $[SO_2]$ and [NO] in the gas streams were controlled at 1000 ppmv and 250 ppmv. respectively. The processing voltage was kept at 25 KV. n_{SO2} and nNO increase with increasing $[H_2O_{(g)}]$ in the gas stream as a result of more efficient generation of OH and HO_2 radicals. With 15 % by volume $[H_2O_{(g)}]$ in the gas stream, more than 95 % NO and 32 % SO_2 in the gas stream were simultaneously removed with DBDs. Under the same operating conditions, the value of nSO_2 is lower than that of n_{NO} due to the higher inlet $[SO_2]$ and lower reaction rate constant between SO_2 and gas phase radicals. Nevertheless, simultaneous removal of SO_2 and NO from gas streams has been achieved with DBDs.

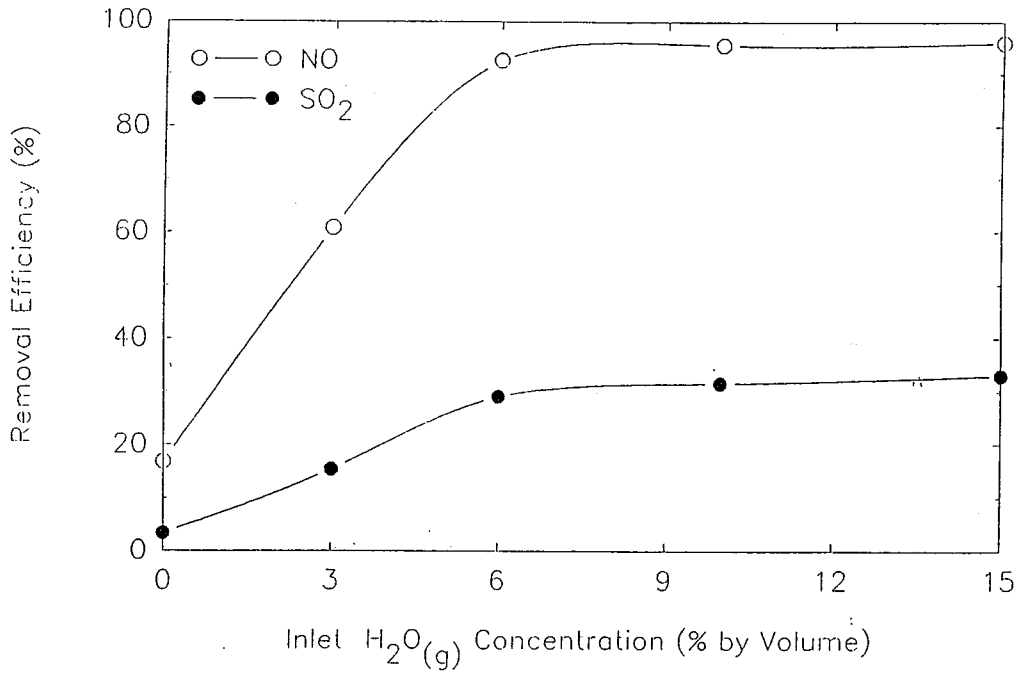


Figure 4 Dependence of η_{so2} and η_{NO} on inlet $[H_2O_{(g)}]$ at 160℃ for gas streams containing 1000 ppmv SO_2, 250 ppmv NO, 6% by volume CO_2, and N_2 as the carrier gas. The applied voltage is 25 KV.

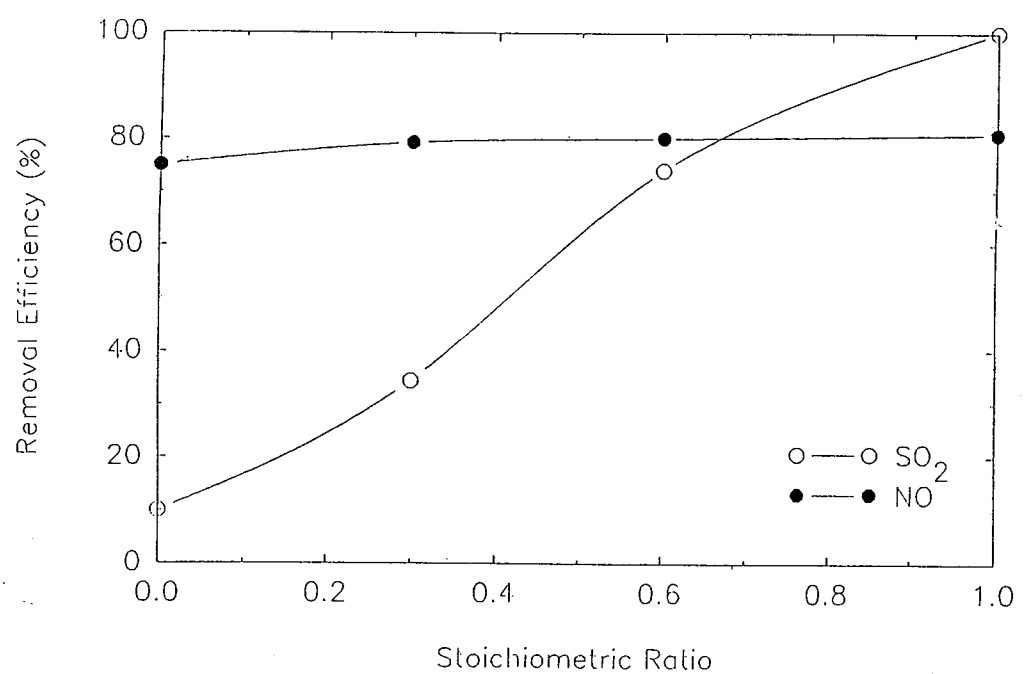


Figure 5 η_{SO2} and η_{NO} as a function of injected NH_3 expressed as stoichiometric ratio (SR) at 130℃. The processing voltage is 25KV. The gas stream is of the composition $SO_2/NO/O_2/H_2O_{(g)}/CO_2 = 0.1/0.025/6/6/12\%$ by volume.

The effect of adding NH_3 to the gas stream on n_{SO2} and n_{NO} was also experimentally determined and is presented in Figure 5. NH_3 was injected downstream of the reactor to chemically neutralize H_2SO_4 and HNO_3 in the gas stream. The gas stream is of the composition $SO_2/NO/O_2/CO_2/H_2O_{(g)}$= 0.1/0.025/6/12/6 % by volume with N_2 as the carrier gas. The temperature was 130 ℃. The amount of NH_3 injected is expressed as stoichiometric ratio (SR) which is defined as in Equation (B).

$$SR = \frac{[\ NH_3\ ]}{2\ [\ SO_2\ ] + [\ NO\ ]} \qquad (B)$$

The above definition is based on the assumption that $(NH_4)_2SO_4$ and NH_4NO_3 are the final product of the neutralization. As SR increases from O to 1, n_{SO2} increases from 10 % to 100 % while n_{NO} is insensitive to NH_3 injection. Significant increase of n_{SO2} with increasing SR is possibly a result of the heterogeneous reactions among SO_2, NH_3, and $H_2O_{(g)}$ rather than the simple chemical neutralization of generated H_2SO_4 with NH_3 (Person *et al.* 1985; Bai *et al.* 1991).

CONCLUSIONS

The effectiveness of using DBDs to remove SO_2, NO, and simultaneously remove SO_2 and NO from gas streams was evaluated experimentally through a laboratory-scale reactor. The results obtained at 160 ℃ showed that SO_2 and NO removal efficiencies were dependent on the applied voltage, and inlet concentrations of $H_2O_{(g)}$ and temperature of the gas stream. Simultaneous removal efficiencies for SO_2 and NO at inlet concentrations of 1000 ppmv and 250 ppmv were as high as 35 % and 90 %, respectively. Higher temperature resulted in higher removal efficiencies due to a higher E/N value. NH_3 injection significantly enhanced SO_2 removal more likely due to the direct thermal reaction between SO_2 and NH_3, rather than the neutralization of H_2SO_4.

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