CORONA ENHANCED ABSORPTION OF SO₂/NO_x

by

Shirshak K. Dhali
Department of Electrical Engineering
Southern Illinois University at Carbondale
Carbondale, Illinois 62901

Final Report
January 1, 1989–August 31, 1990

Submitted to
U.S. Department of Energy
Contract Number DE-FC22-89PC89904

November 1990

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This report contains results of an investigation of plasma-assisted oxidation of SO_2 to SO_3 . The SO_3 is a more desirable by-product of flue gas than SO_2 because it easily dissolves in water and can be reacted with lime to form gypsum. A coaxial dielectric-barrier discharge is used to generate an air plasma to carry out the reaction. The dielectric-barrier discharge, which is an interrupted discharge, is very efficient in producing atomic oxygen and requires a simple form of excitation. We have observed a significant reduction (over 75%) in the SO_2 concentration using this technique. The simulation results indicate that about 99% of the SO_2 can be oxidized with UV-irradiation along with plasma oxidation and that NO_x can be reduced to N_2 in the presence of an air plasma. The results of varying the gas composition, the gas pressure, and the gas flow are also reported.

INTRODUCTION

The removal of sulfur is of great importance to the utilization of coal as a fuel. Physical cleaning alone will not produce a coal that complies with the federal emission limits; therefore, the efficient removal of sulfur compounds from combustion and conversion facilities is all the more important. This is evident from the renewed interest in finding alternative methods for the removal of noxious products from flue gas. The Electric Power Research Institute (EPRI) has set a goal to develop and demonstrate SO₂ control technology which can achieve 50 to 70% SO₂ removal at costs of \$500 to \$1,000/ton of SO₂.

Scrubbers or solid sorbents are commonly used to remove SO₂ and other noxious products from flue gas (Klingspor and Cope 1987). The three most common post combustion flue gas desulfurization technologies are wet scrubbing, spray drying, and dry scrubbing (Markussen and Pennline 1989). These techniques efficiently remove SO₂ from flue gases, but the waste disposal produces additional problems. The removal of NO_x gases is performed by a separate process, selective catalytic reduction, which uses ammonia reagents to convert nitrogen oxides to atmospheric nitrogen. No reliable chemical methods have yet been developed for simultaneous removal of both SO₂ and NO_x gases in one single-stage process.

Although there are only a few pilot plants using electrical energy for the desulfurization of flue gas, there is considerable interest in investigating this novel and alternative technology (Klingspor and Cope 1987). Most of the investigations using electrical energy are based upon either corona discharges (ac, dc, and pulsed) or electron beam excitation (Mizuno et al. 1986, Frank et al. 1987).

In most electrical energy-related schemes, the electrons from either a high-energy electron beam (400-800 keV) or a corona discharge are used to excite, dissociate, and ionize gas molecules to produce radicals (O, OH⁻, HO₂, etc.). The

radicals react with SO_2 and form aerosols, which can either be collected by an electrostatic precipitator or easily dissolved in water (Mizuno et al. 1986). Though the electron-beam process has an advantage over scrubbers, it requires many accelerators that are capital-intensive, and X-ray shielding is necessary. The use of corona discharge is energy inefficient and the performance is poor. The poor performance is probably due to the small ionization region of coronas, and the power efficiency is low because a large amount of energy goes into gas heating.

Mizuno et al. (1986) and Clements et al. (1989) have demonstrated that a pulsed streamer corona produces energetic electrons that excite, dissociate, and ionize gas molecules, forming radicals that enhance the gas-phase chemical reactions which convert SO_2 to acid mist and/or particulate aerosols. The SO_2 removal efficiency was compared with that of the electron-beam and dc corona flue gas treatment processes. The pulsed corona technique was found to be more efficient.

In this paper we report the application of a dielectric-barrier discharge, also known as silent discharge, for the removal of SO_2 from flue gas. The dielectric-barrier discharge is widely used in industry for ozone synthesis and as an excimer UV source (Eliasson et al. 1987, 1984). This discharge is intermittent and the current exhibits a large number of spikes during that part of the voltage period when the discharge is on. Experimental investigations in atmospheric air have shown that the current flows on a large number of microdischarges (Eliasson et al. 1987, 1984). Because of the high field during these microdischarges, the average electron energy is higher than dc, rf, or microwave discharges. This is the primary basis for proposing the use of dielectric-barrier discharge for plasma processing of SO_2 which requires energetic oxygen atoms.

The plasma produced by electrical discharges can be divided into two types. The first is the "hot" or "equilibrium" plasma, which is characterized by a high gas temperature and approximately equal gas and electron temperatures. Typical

examples of such plasma are those produced in arcs and plasma torches. The second type of plasma is termed "low temperature" or "non-equilibrium" plasma and is characterized by low gas temperature and a high electron temperature (Hollahan and Bell 1974).

Various low-temperature plasma chemical reactions have been applied to gas-phase toxic decomposition (Baillin and Hertzler 1978). The plasma used for these processes are produced by dc, rf, or microwave discharges (rf plasma being the most popular). These discharges are usually operated at low pressures (in the hundreds of mTorr range) in order to obtain a stable discharge. The electron density in such weakly ionized discharges is of the order of 10^{10}cm^{-3} , and the electron temperature is of the order of 1 to 3 eV.

We have used a dielectric-barrier discharge to generate a non-equilibrium plasma, at atmospheric pressure, to process SO_2 and NO_x into products that are easy to remove. The SO_2 in the presence of the plasma is oxidized to SO_3 . This removal process is further enhanced by irradiating the processed gas with low levels of UV radiation (250 nm). The nitrogen oxides in the presence of the air plasma will be converted to atmospheric nitrogen. The SO_3 is easily removed when dissolved in water, reacted with ammonia, or by an electrostatic precipitator. Although plasma generated by microwave and corona have been investigated, the use of dielectric-barrier discharge has several advantages over other schemes. The dielectric-barrier discharge produces a stable and uniform plasma at or near atmospheric pressures with very high electron energies (Eliasson and Kogelschatz 1988). The high energy electrons are responsible for producing active species in the plasma that react with SO_2 and NO_x .

THE MODEL

The efficiency of generating atomic oxygen and ozone in a dielectric-barrier discharge has been studied by several researchers (Eliasson and Kogelschatz 1988, 1986). The atomic oxygen is produced mainly by electron impact excitation from the ground state, such as:

The dissociation rate coefficient for oxygen has been calculated and measured as a function of E/N (reduced electric field) by several researchers. The efficiency of oxygen atom production with respect to the energy used is only weakly dependent on E/N in the range 100 to 300 Td and drops considerably at lower E/N. While there is no point in trying to go to extremely high E/N values, it is important to interrupt the discharge before the reduced field falls much below $E/N = 10^{15} \text{ Vcm}^2$ (100 Td), and it can be assumed that pulsing helps in this respect.

Although several researchers have attempted to use plasmas in various forms there is a complete lack of characterization and modeling of a flue gas plasma. The presence of SO_2 and NO_x will modify the composition of an air plasma. If further meaningful contribution is to be made in this area, the plasma with SO_2 and NO_x has to be characterized and modeled.

The existing models for the silent and the dielectric-barrier discharge are very approximate due to the random nature of the microdischarges. However, some

work in the area of modeling impulse corona for flue gas treatment has been done by Gallimberti (1988) (Atkinson et al. 1989).

The important electron impact processes taken into account for the discharge kinetics are:

Furthermore, for the complete description of the plasma chemistry, the molecule-molecule reactions listed below have been included in the model. These reactions and the rate coefficients are fairly exhaustive, and have been obtained from current literature on atmospheric chemistry.

In all reactions involving the third body, M refers to either N₂ or O₂ and the rates are approximately the same for both. Since the O₂-O bond strength is only 1 eV, with UV radiation (200 to 300 nm) there are two significant photodissociative channels for O₃, (Slanger et al. 1988)

The excess photon energy in each case goes into forming excited oxygen molecules. The excited oxygen molecules go through further photodissociation,

The overall reaction of ozone with UV is given by:

Since the microdischarges are best characterized as streamers, the typical electron density at atmospheric pressure is of the order of $0.5 \times 10^{14} \text{ cm}^{-3}$ (Dhali and Williams 1987). The typical duration of these streamers is of the order of 2 to 10 ns for a 1 cm gap (Dhali and Williams 1987). Using the above model, simulations were carried out to study the time evolution of the species and the effect of UV-irradiation on the species population. For these simulations, the total pressure at room temperature was 760 Torr, with approximately 80% N_2 , 20% O_2 , 1000 ppm of SO_2 and NO , and 500 ppm of N_2O . This is representative of a flue gas, except that O_2 concentration tends to be lower in actual flue gas.

The species concentration as a function of time is shown in figures 1 and 2 for without and with UV irradiation, respectively. The simulations suggest that with adequate residence time (100 μs) over 95% of the SO_2 is oxidized to SO_3 , and NO and N_2O are completely reduced to N_2 . Furthermore, the UV-irradiation in low levels is very effective in dissociating ozone, produced in the discharge, to atomic oxygen. This enhances the oxidation of the SO_2 and over 99% removal can be achieved with 10 W/cm^2 of UV-irradiation and residence time of the order of 10^{-3} s .

EXPERIMENTAL RESULTS AND DISCUSSIONS

Although parallel plate electrodes have been used for the generation of ozone (Eliasson et al. 1987) we choose a coaxial geometry for which the active volume is well defined. The schematic of the experimental set-up is shown in Figure 3. The discharge chamber (Figure 4) consists of a stainless steel center electrode, a glass dielectric, and an aluminum outer electrode. For the dimensions shown in Figure 4, the gap capacitance is calculated to be $5.5 \times 10^{-12} \text{ F}$.

The power supply consists of a 110 V to 15 kV transformer which is excited by the line voltage. For a 60 Hz power supply and at the peak voltage, the capacitive current is approximately 0.6 mA. This small current does not cause a significant

Figure 1. Time evolution of species concentration without UV radiation.

Figure 2. Time evolution of species concentration with UV radiation.

Figure 3. Schematic of the experimental set-up.

Figure 4. Schematic of the discharge chamber.

voltage drop across the series resistor of 50 Ω . The voltage waveform for a typical dielectric-barrier discharge is shown in Figure 5. The microdischarges appear on the rising edge of the voltage waveform and as the dielectric charges up the discharge is quenched. The negative going pulse discharges the dielectric and the cycle continues.

The gas flow is controlled by a set of MKS mass flow controllers. The on-line diagnostics consist of a Thermo-Electron Model 40 pulsed fluorescent SO_2 analyzer and a SPEX-50M spectrometer. The pulsed fluorescent analyzer requires a minimum flow of 1400 SCCM and can detect SO_2 down to 1 ppm.

The effect of discharge parameters such as discharge voltage, gas composition, gas flow, and gas pressure on the removal of SO_2 has been studied. We have also studied the emission spectra in order to identify the reaction pathways. The experiments were done at room temperature for a pressure range of 650 to 760 Torr, total flow rates in the range of 1550 to 3500 SCCM, and SO_2 concentration in the range of 300 to 14,000 ppm. The applied voltage in all cases was a 60 Hz sinusoidal of 24 kV (peak-to-peak).

The concentration of oxygen in the reactor plays an important role in the removal of SO_2 . The percentage of SO_2 removal for various oxygen flow rates is shown in Figure 6. A SO_2 concentration of 3590 ppm in N_2 was used. The applied voltage was 24 kV peak-to-peak, and the discharge pressure was 650 Torr. The SO_2 is oxidized to SO_3 by the three body reaction in reaction V, and the reaction rate at room temperature $K_1 = 8.2 \times 10^{-32} \text{ cm}^6/\text{s}$ (Singleton and Cvetonovic 1988). The oxygen atoms are produced by electron impact dissociation given by reactions A and B, and the overall rate coefficient $K_2 = 2.0 \times 10^{-9}/\text{s}$ (Dutton 1975). The other important reactions involving oxygen atoms are reactions G and H with a rate coefficient $K_3 = 5.5 \times 10^{-34} \text{ cm}^6/\text{s}$ and $K_4 = 8.8 \times 10^{-15} \text{ cm}^3/\text{s}$, respectively (Arnold and Comes 1979).

Figure 5. Voltage waveform of a typical discharge in a dielectric barrier.

Figure 6. The percentage SO₂ removal for a pressure of 650 Torr and an applied voltage of 24 kV peak-to-peak. The initial concentration of SO₂ was 3950 ppm in N₂. The N₂ flow was (a) 2500 SCCM, (b) 3000 SCCM, and (c) 3500 SCCM.

Since the concentration of O_3 is orders of magnitude smaller than O_2 , the loss of O through reaction H is not important. Therefore, the two competing loss mechanisms for oxygen atoms are reactions G and H. The resulting rate equations are:

$$dn_O/dt = 2K_2 n_{O_2} n_e - K_1 n_O n_{SO_2} (n_{O_2} + n_{N_2}) - K_3 n_O n_{O_2} (n_{O_2} + n_{N_2}) \quad (1)$$

and

$$dn_{SO_3}/dt = K_1 n_O n_{SO_2} (n_{O_2} + n_{N_2}) \quad (2)$$

where: n_e = electron,
 n_O = oxygen atom,
 n_{O_2} = oxygen molecule,
 n_{N_2} = nitrogen molecule,
 n_{SO_2} = SO_2 density, and
 n_{SO_3} = SO_3 density.

Assuming that oxygen atoms reach a quasi-steady state, density can be obtained from equation 1:

$$n_O = 2K_2 n_{O_2} n_e / (K_1 n_{SO_2} + K_3 n_{O_2}) (n_{O_2} + n_{N_2}) \quad (3)$$

Substituting the value of n_O in equation 2, the rate for the conversion of SO_2 to SO_3 is given by:

$$dn_{SO_3}/dt = 2K_1 K_2 n_e n_{SO_2} n_{O_2} / (K_1 n_{SO_2} + K_3 n_{O_2}) \quad (4)$$

The addition of oxygen molecules increases the oxygen atom concentration (reaction E). This initially increases the percentage of SO₂ removal as shown in Figure 6. However, further increase in O₂ concentration favors ozone formation (reaction G) and thus depletes the atomic oxygen concentration. It is evident from equation 4 that at high O₂ concentration, the rate of SO₃ formation becomes independent of the O₂ concentration. For O₂ in air proportion, the percentage SO₂ removal is well in the saturation region (approximately 500 SCCM in Figure 6). The plots for three different flow rates are shown in Figure 6. For the slower flow rate (Figure 6a) residence time increased and the percentage reduction is higher.

We also studied the effect of SO₂ concentration on SO₂ removal. For these experiments the N₂ and O₂ concentrations were kept constant. The results for N₂ to O₂ in air proportions are shown in Figure 7. During the experiment the pressure and voltage were maintained at 650 Torr and 24 kV peak-to-peak, respectively. Since SO₂ is an attaching gas, at high concentrations it reduces the electron density, n_e . This results in the lowering of SO₂ removal at high SO₂ concentration. The drop in the SO₂ removal, shown in Figure 7, occurs for SO₂ concentration greater than $(K_3/K_1)n_{O_2}$. At low SO₂ concentration, the percentage of SO₂ removal is higher. In flue gas resulting from coal-fired plants, the SO₂ concentration falls well into the high removal region.

Emission spectra from a dielectric-barrier discharge in pure O₂ and an O₂ and SO₂ mixture are shown in Figure 8. The purpose of the spectroscopy was to verify that reaction V was indeed one of the reaction pathways for the removal of SO₂. Due to the high pressure and random nature of the discharge, the interpretation of the spectra becomes difficult. However, the oxygen atom emission line at 7775° A in Figure 8 clearly shows a reduction in intensity with the addition of SO₂.

Figure 7. The percentage SO₂ removal as function of SO₂ flow for a total flow of (a) 3500 SCCM, (b) 3000 SCCM, and (c) 2500 SCCM. The discharge pressure was 650 Torr and the discharge voltage was 24 kV peak-to-peak.

Figure 8. Emission spectra of a dielectric-barrier discharge for (a) O_2 and (b) 1% SO_2 in O_2 . The discharge pressure was 650 Torr and the discharge voltage was 24 kV peak-to-peak.

CONCLUSIONS

This method is a novel, viable, and efficient means of SO_2/NO_x removal from combustion and conversion facilities. It is applicable over a wide range of pressures and temperatures and does not require any material regeneration, which is a major advantage over solid sorbents. The plasma produced by a simple voltage transformer at 60 Hz (power supply voltage) is an effective and inexpensive source of plasma to carry out gas-phase reactions of SO_2 and NO . The resulting by-products could possibly be useful if the concentration of the mixed acids is high enough or gypsum is produced. In addition, this is the first effort towards modeling the flue gas chemistry in a plasma. The simulation results suggest UV irradiation will further enhance the removal of SO_2 and NO_x . The simultaneous removal of NO_x will make this an attractive alternative to other flue gas clean up methods.

We have shown that the dielectric-barrier discharge has the potential for removing sulfur from flue gas. Since the rate, K_2 , is strongly dependent on the electric field, the dielectric-barrier discharge due to the high reduced field, E/N , is an efficient means for the production of atomic oxygen and atomic nitrogen.

REFERENCES

- Arnold, I., and F. J. Comes. 1979. Chemical kinetic data for atomic oxygen. Journal of Chemical Physics 42:231.
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe. 1989. Evaluated kinetics and photochemical data for atmospheric chemistry, Supplement II 18:882-958.
- Baillin, L. J., and B. I. Hertzler. 1978. Environmental Science and Technology 12:673.
- Clements, J. S., A. Mizuno, W. Finney, and R. H. Davis. 1989. IEEE Transaction on Industrial Application 25(1):62.
- Dhali, S. K., and P. F. Williams. 1987. Journal of Applied Physics 62:12, 4696.
- Dutton, J. 1975. A survey of electron swarm data. Journal of Physical and Chemical Reference Data 4(3):577.
- Eliasson, B., M. Hirth, and U. Kogelschatz. 1987. Ozone synthesis from oxygen in dielectric barrier discharge. Journal of Physics D: Applied Physics 20:1, 21-1437.
- Eliasson, B., V. Kogelschatz, and P. Baessler. 1984. Dissociation of O₂ in N₂/O₂ mixtures. Journal of Physics B: Atomic and Molecular Physics 17:L797-L801.
- Eliasson, B., and U. Kogelschatz. 1988. Journal of Physics B: Applied Physics 46:299.
- Eliasson, B., and U. Kogelschatz. 1986. Journal of Physics B: Applied Physics 19:1241.
- Frank, N. W., G. A. Miller, and D. A. Reed. 1987. Operating and testing a combined SO₂ and NO_x removal facility. Environmental Progress 6(3):177-182.
- Gallimberti, I. 1988. Pure and Applied Chemistry 60:663.
- Hollahan, J. R., and A. T. Bell. 1974. Techniques and application of plasma chemistry. New York: John Wiley and Sons.
- Klingspor, J. S., and D. R. Cope. 1987. FGD handbook, flue gas desulfurization systems. London: International Energy Association Coal Research.
- Markussen, J. M., and H. W. Pennline. 1989. In Proceedings of the 6th Annual International Pittsburgh Coal Conference, p. 299. Greensburg, Pennsylvania: MEMS.
- Mizuno, A., J. S. Clements, and R. H. Davis. 1986. A method for the removal of sulfur dioxide from exhaust gas utilizing pulsed streamer corona for electron energization. In IEEE Transaction on Industrial Application, vol. 22, pp. 516-522.
- Singleton, D. L., and R. J. Cvetonovic. 1988. Evaluated chemical kinetic data for the reaction of atomic oxygen with sulfur containing compounds. Journal of Physics and Chemistry, Reference Data 17(4):1377-1390.
- Slanger, T. G., L. E. Jusinski, G. Black, and G. E. Gadd. 1988. Science 241:945.

END

DATE FILMED

01 / 15 / 91