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OFFICE OF RESEARCH ADMINISTRATION  
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Date: June 2, 1972

Project Title Research Initiation - Application of High Voltage Electric Fields to  
the Removal of SO<sub>2</sub> and NO<sub>2</sub> from Combustion Effluent

Project No: E-19-604 (Old B-514)

Principal Investigator: Dr. Michael J. Matteson

Sponsor: National Science Foundation

Effective Termination Date: March 31, 1972

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☒ Final Fiscal Report before June 30, 1972

Assigned to: School of Chemical Engineering

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GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

March 30, 1972

E-19-604



Dr. R. V. Jelinek  
Engineering Division  
National Science Foundation  
Washington, D. C. 20550

Dear Dr. Jelinek:

This letter is intended as a final technical report on NSF Research Initiation Grant No. GK-5531, "Application of High Voltage Electric Fields to the Removal of  $\text{SO}_2$  and  $\text{NO}_2$  from Combustion Effluent", awarded to Michael J. Matteson at Georgia Institute of Technology, April 1, 1970 and completed March 31, 1972.

A manuscript entitled "The Corona Discharge Catalysis of Sulfur Dioxide" based on work performed under this grant in collaboration with graduate students Mr. Hugh L. Stringer and Mr. Walter L. Bush, has been submitted to Environmental Science and Technology, December, 1971.

Another manuscript, "The Absorption of Sulfur Dioxide by Electrically Charged Water Droplets" is in preparation. The enclosed paper "The Separation of Charge at the Gas-Liquid Interface by Dispersion of Various Electrolyte Solutions", was based on work partially supported by this grant and was published in J. Coll. and Interface Sci., 37 No. 4, December 1971. Mr. Busbee's Master's Thesis in Chemical Engineering "Chemical Reaction and Nucleation Rates in the Corona Discharge Catalysis of  $\text{SO}_2$  in Humid Air Streams", Georgia Institute of Technology, October, 1971, was based on work supported by the same grant.

A description of the work is contained in the enclosed manuscript. Comments by you regarding the interest of NSF in supporting further work in this area would be sincerely appreciated. I believe that the results are applicable to basic electrostatic precipitator technology. For instance we have shown probable mechanisms for pollutant gas-corona discharge reactions for the specific case of  $\text{SO}_2$ .

The results indicate those conditions which promote sulfuric acid mist formation in an electrical discharge. This information is useful in precipitator design since discharge of sulfur trioxide or sulfuric acid mist is highly undesirable. In addition corona reactions with other gases may increase the output of pollutants in a more oxidized, and toxic state. Further work needs to be done to identify what types of nitrogen oxide reactions are promoted in precipitators and what operating characteristics can be used to control these reactions.

Thank you for your interest and support.

Sincerely yours,

Michael J. Matteson  
Assistant Professor

MJM:np

E-19-604

~~6-23-65~~

CORONA DISCHARGE OXIDATION OF SULFUR DIOXIDE

by

Michael J. Matteson, Hugh L. Stringer<sup>1</sup>, and Walter L. Busbee<sup>2</sup>



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# ABSTRACT

Sulfur dioxide (500-3000 ppm) in a flowing humid air mixture was exposed to a corona discharge in a wire-to-cylinder reactor. Sulfuric acid mist was precipitated on the inside wall-electrode; and ozone and the remaining  $\text{SO}_2$  were monitored at the exit port.

Residence times, humidities, oxygen and  $\text{SO}_2$  concentrations were varied to study the kinetics of the conversion of  $\text{SO}_2$  to acid mist. The reaction was zero order with respect to  $\text{SO}_2$  in the range tested, and the rate determining step appeared to be the formation of atomic oxygen by the electrical discharge. Optimum reaction rates occurred at 70% relative humidity and above 15% oxygen concentration. Studies of the precipitated droplets indicated a mean size of  $6.36\mu$  before deposition.

## INTRODUCTION

Sulfur dioxide mixed with oxygen or air has been oxidized in the presence of an electrical corona discharge by a number of investigators. Miklos et al. (1966) reported efficiencies on the order of 35% for direct oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in an air stream. Palumbo and Fraas (1971) concluded that a damped or pulsed high frequency current was more effective than direct current for  $\text{SO}_2$  conversion. In their tests the reactor was placed in an oven at  $130^\circ\text{C}$ , and a conversion efficiency of 96% was obtained with a power expenditure of 9 watts over a period of 30 minutes. In the absence of water vapor, only 67% of the  $\text{SO}_2$  was converted. Reaction products were identified as elemental sulfur and sulfuric acid. The reaction mechanism was not studied.

Moyes and Smith (1965) presented comparative results for the thermal-and electrical discharge-activation of mixtures of  $\text{SO}_2$  and  $\text{O}_2$ . They showed that the activation by electrical discharge was more efficient, but had doubts about its industrial application for exothermic reactions for which a suitable catalyst was available.

Several questions as to the various reaction mechanisms in such a gas mixture exposed to a corona must be dealt with before launching into pilot scale studies. However, in the case of  $\text{SO}_2$ , such information is useful especially in certain electrical precipitator operations. The generation of sulfuric acid mist in limited quantities, in power plant stack gases, may have the beneficial side-effect of combining with and reducing the resistivity of some types of fly ash, thereby increasing the precipitator's efficiency. Overproduction of the mist, however,

would initiate corrosion problems and decrease the overall performance of the precipitator in the long term. Reese and Greco (1968) have shown in tests with TVA precipitators that the presence of  $\text{H}_2\text{SO}_4$  mist seriously lowered the collection efficiency of electrostatic precipitators. Therefore, it is desirable to have a quantitative estimate of the extent to which various operating conditions in a corona discharge contribute to the conversion of  $\text{SO}_2$  to sulfuric acid mist. This paper treats several of the parameters influencing the  $\text{SO}_2$  oxidation in a corona to include relative humidity, electrical potential, gas concentrations and flow rates; and reaction mechanisms are proposed, based on results of these studies.

Preliminary tests were made using a small point-to-plane electrostatic precipitator described by Morrow and Mercer (1964). A stream of air at 95% relative humidity and 4.0 ppm  $\text{SO}_2$  flowed through the electrical field at a rate of 22 l/hr. A potential of -8.0 KV was applied for 120 seconds across the 1.0 cm gap. The  $\text{SO}_2$  was completely removed from the air. The main phase of this study was directed toward concentrations of  $\text{SO}_2$  in the 500-2000 ppm range and much larger volumetric flow rates (1 - 5 l/min). It was decided to try a wire-to-cylinder type electrical field and to measure  $\text{SO}_2$  removed in a dynamic situation at 20°C.

#### EXPERIMENTAL ARRANGEMENT

The experimental apparatus is shown schematically in Figure 1. Regulated compressed air was directed through activated charcoal, and a nitrocellulose membrane filter. The air stream is then split; one branch feeds directly into a glass humidifier column, the other through

a flow gauge. The two streams are rejoined in a condensate trap/mixing chamber. The mixed air stream flows through a second flow gauge and meets the sulfur dioxide. It was possible to inject a constant low-volume flow of  $\text{SO}_2$  into the main stream by means of a high pressure drop capillary coil connected by a tee to the main line. By varying the pressure on the coil from 6 to 22 psig, the  $\text{SO}_2$  injection rate could be varied from 2.5 to 25.0 ml/min corresponding to concentrations in the gas stream from 500-5000 ppm.

The dry bulb temperature of the humidified gas mixture was measured with a total immersion thermometer and the dew point was monitored with a Cambridge Systems Model 880, Thermoelectric Dew Point Hygrometer. A remote thermistor, connected to the hygrometer, measured the bulk gas temperature of the reactor effluent.

The corona discharge reactor design is similar to a tubular electrostatic precipitator. Details of the construction are shown in Figure 2. The outer grounded electrode is a stainless steel tube, 2-inches I.D. and 1/16-inch wall thickness. The tube ends are slotted for "O"-rings which provide a gas-tight seal with the grooved end plates. The inner, negative electrode is a 32-mil nichrome wire. Direct current was supplied to the wire by a Beckman, Model 6205-5MA-M, high voltage, DC power supply. The power unit was continuously variable between 0-25 KV. A 0-1.2 ma ammeter registered the current flow across the wire-cylinder field. A standard threaded electrical connector provided contact between the coaxial wire and the negative terminal of the power supply unit. Auxiliary circuitry was added to reduce the total current flow to less than one ma.



The sulfur dioxide concentrations of the gas mixture was monitored with a Beckman Model 215A Infrared Analyzer. About 100 ml/min of reactor effluent was diverted through a helical glass coil immersed in an ice-acetone bath to remove moisture from the sample stream, and then a guard filter before entry into the analyzer. A continuous read-out of the  $\text{SO}_2$  concentration was recorded on a strip chart. The error in the  $\text{SO}_2$  determination was on the order of  $\pm 5.0$  percent. Dry air produced an IR scale deflection equivalent to 25-50 ppm  $\text{SO}_2$ . Additional errors due to the presence of water vapor in the sample stream were eliminated by the cold trap.

Ozone generated in the reactor was determined using a modified ASTM Procedure D1609-60 (1964). A portion of the reactor effluent was bubbled through 100-200 ml of alkaline KI absorbing solution and the absorbance of the solution was measured at 352 microns with a Beckman DU Spectrophotometer.

#### OPERATING PROCEDURE

A kinetic study of the corona-sulfur dioxide reaction was conducted by measuring the loss in  $\text{SO}_2$  during a given residence period of the gas mixture flowing through the reactor. The initial  $\text{SO}_2$  concentration could be held at a fixed value while the gas stream volume was varied, thus varying the residence time. Also the  $\text{SO}_2$  concentration could be varied for a fixed volumetric flow rate.

The relative humidity of the mixed gas stream was controlled by adjusting the ratio of dry to saturated air stream flow rates. When initial  $\text{SO}_2$  concentration, air humidity, flow rate and temperature reached

the desired constant values (1.5-2 hours), the power was applied and the concentration of  $\text{SO}_2$ , as recorded by the IR, was observed to drop until it reached a lower constant value. Approximately five minutes elapsed before steady-state reaction conditions were attained in the reactor and registered by the IR. The power supply voltage, corona current, and the  $\text{SO}_2$  concentration were continuously recorded. After the  $\text{SO}_2$  concentration reached a lower stable value, the power supply was cut off and the system allowed to return to non-reaction conditions to insure that the initial  $\text{SO}_2$  concentration had not changed. The system was sensitive to leaks in the gas conveying apparatus and seals had to be checked before each run.

The infrared analyzer was calibrated before each experiment over the ranges 0-1000 ppm and 0-5000 ppm  $\text{SO}_2$ . Dry nitrogen was used as a zero gas and calibrated gas mixture (Matheson) of 5162 ppm  $\text{SO}_2$  in  $\text{N}_2$  provided the span gas.

ASTM Procedure D-1609-70 had to be modified to measure the relatively high  $\text{O}_3$  concentrations produced in the reactor. The ozone generation was determined first in a series of blank runs with only humidified air flowing through the energized reaction zone. The gas flow rate was varied from 0.5 to 5.0  $\ell/\text{min}$ , and the relative humidity was maintained constant at about 70%. The reactor effluent was bubbled through a coarse gas dispersion tube immersed in 100-200 ml of alkaline KI solution. It was necessary to dilute the absorbant solution by as much as ten-fold before continuing with the ASTM procedure. Also, it was necessary to use 30% by weight  $\text{H}_2\text{O}_2$  rather than the standard 3% in order to obtain stabilized absorbance readings. The instability problem was thought to be a result

of the presence of interfering oxides of nitrogen generated in the reactor and picked up in the absorbing solution. Ozone measurements were also made in the presence of  $\text{SO}_2$ .

Sulfuric acid mist was formed in the reactor by the hydration and nucleation of sulfur trioxide in the humid air stream. The mist was deposited on the inside grounded wall of the cylinder due to the action of the electric field. The size of the deposited droplets was determined according to the method of Horstman and Wagman (1967). Glass microscope slides (0.7 cm x 7.62 cm) were coated with a thin film of reagent grade iron in a Kinney vacuum evaporator. The iron film thickness was on the order of  $0.5\mu$ . The metal coated slides were then placed length-wise along the wall of the reactor. Acid droplets deposited on the metal film left an etched replica, which could be viewed by light or electron microscopy. Photographs were made and size analysis performed with a Zeiss TGZ-3 Particle Size Analyzer. The acid content of the reactor residue was determined by disassembling the reactor after a test and washing with 400-500 ml of deionized water. The acid concentration of the wash was then measured with a pH meter and checked by titration with a standardized NaOH solution, using Bromthymol Blue as an indicator.

## RESULTS

### Reaction Kinetics

The rate of disappearance of  $\text{SO}_2$  appeared to be zero order with respect to  $\text{SO}_2$  for those initial concentrations investigated. Figure 3 shows initial reaction rates for  $\text{SO}_2$  concentrations between 500 and 3000 ppm. The rate of  $\text{SO}_2$  removal appeared to reach a steady state value after

the first 1.5 minutes. These tests were made with air at 70% relative humidity.

We decided to test at the 70% level after a series of experiments at various humidities (Figure 4) showed that the removal rate was an optimum for that particular water vapor content. At higher humidities the dielectric properties of the gas were probably altered, and corona breakdown and sparkover frequently occurred. During a test at 70% RH the temperature of the reactor effluent increased by  $6.3^{\circ}\text{C}$  for the 2.5 min residence time. This was a result of the dielectric heating by the electric discharge and the exothermic nature of the chemical reaction. The humidities reported are therefore inlet values. The variation in initial humidity values was  $\pm 2.0\%$ .

The effect of oxygen concentration on reaction rate was quite significant below 15% for an initial  $\text{SO}_2$  concentration of 1000 ppm (Figure 5). In these tests the gas flow rate was held constant at 5.0 /min and the  $\text{O}_2$  concentration varied from 0-21% by diluting the primary air stream with nitrogen. Sulfur dioxide was not removed when oxygen was absent from the gas mixture. At oxygen concentrations above 15%, the  $\text{SO}_2$  removal rate appeared to be constant.

The kinetics of  $\text{O}_3$  formation in the corona discharge reactor was investigated in the presence and absence of  $\text{SO}_2$ . All tests were conducted with air at 70% RH. These data are presented in Figure 6. In comparing those tests where 1000 ppm  $\text{SO}_2$  was present with tests which included no  $\text{SO}_2$ , one can see that practically all of the ozone generated by the discharge is absent in the  $\text{SO}_2$  oxidation reaction. The error in the  $\text{O}_3$  determination is approximately  $\pm 10\%$  for the flow rates discussed.



This was due mainly to variations in the corona discharge characteristics at the 70% relative humidity of the air stream.

#### Power Utilization

A series of experiments was conducted to determine the specific energy consumption as a function of flow rate,  $\text{SO}_2$  removed, and applied power. The effects on power consumption of wall loading as a result of the precipitation of acid droplets was also investigated. Figure 7 shows the effect of various power levels on the  $\text{SO}_2$  exit concentration for three flow rates. The  $\text{SO}_2$  concentration drops off rapidly with corona onset, and the curves indicate that application of sufficient power would result in essentially complete removal of  $\text{SO}_2$ . For the 0.5 l/min flow rate, the extrapolated value of 15 watts represents total  $\text{SO}_2$  removal. This is equivalent to 0.015 KWH/SCF (15 KWH/1000 ft<sup>3</sup>) or about one sixth the power requirement obtained by Browne and Stone (1965) with a cylindrical quartz reactor.

In an effort to determine the rate at which power consumption varies during reactor operation, the discharge was operated continuously for 240 minutes. The power required to remove 87.5%  $\text{SO}_2$  from a stream flowing at 0.5 l/min at 1000 ppm initial  $\text{SO}_2$  concentration increased by about 20% in the first 100 minutes and then stabilized at 0.0134 KWH/SCF (Figure 8). Decreases in reactor efficiency were much more noticeable if a surface film was allowed to form on the inside wall of the reactor between runs. In two experiments, we compared the results of untreated reactor walls with a second run wherein the walls were etched with concentrated hydrochloric acid prior to the test. In both cases a gas flow of 1 l/min at 70% relative humidity and 1000 ppm  $\text{SO}_2$  was exposed to the

corona for a period of 30.0 minutes. The power consumption dropped from 0.0055 to 0.0050 KWH/SCF in going to the etched tube. In addition the fraction of  $\text{SO}_2$  recovered increased from 32.5 to 50% on a steady state basis. Therefore all tests were repeated and the results reported here reflect the  $\text{SO}_2$  removal rates for the reactor which had been thoroughly cleaned prior to each reaction.

#### Acid Mist

Sulfuric acid mist formed in the reactor by the hydration of  $\text{SO}_3$  and deposited on the reactor wall by the electrostatic field was sampled for particle size analysis. A total of 3215 particles were counted and sized from 32 photographs over 8 segments of microscopic slides. The photos were taken at a total magnification and enlargement of 239 X. The etched imprints were sized and this data was used to estimate the original droplet diameter. The size distribution for the deposited droplets displayed a log-normal probability pattern as shown in Figure 9. The geometric mean diameter,  $D_{gc}$ , was  $23.1\mu$ , and the standard deviation,  $\sigma_{gc}$ , was 2.18. The size of the impacted droplet was essentially random with respect to where the samples were taken in the tube; there was no correlation of size with distance down the tube. It appeared then that nucleation occurred along the entire length of the reactor, and that the particles did not travel far, in the axial direction before being deposited on the wall. Knowing the time elapsed during the deposition of the counter particles, and the area over which these particles fell, the particle deposition rate PDR, could be calculated. This amounted to  $10^4$  particles/cm<sup>2</sup> min or  $0.8 \times 10^6$  particles/min for the whole tube. Assuming that the  $\text{SO}_2$  removal rate is equivalent to the  $\text{H}_2\text{SO}_4$  production

rate,  $W_{H_2SO_4}$ , and that all of the acid formed becomes acid nuclei, a loss of 555 ppm  $SO_2$  in a 1 l/min stream would produce  $1.32 \times 10^{-3} \text{ cm}^2 H_2SO_4/\text{min}$ . Therefore, the theoretical volume of the mean sized droplet before impaction is

$$V_{\text{drop}} = \frac{W_{H_2SO_4}}{\text{PDR}} = 1.35 \times 10^{-10} \frac{\text{cm}^3}{\text{particle}} \quad (1)$$

This is equivalent to an average diameter of  $6.36 \mu$ .

In five separate tests we compared the  $SO_2$  disappearance as measured by the IR, with the  $H_2SO_4$  formed in the reactor and cold trap, as measured by titrimetric techniques. The results showed that about 75% of the  $SO_2$  removed was present in the form of  $H_2SO_4$ . This may have been a result of reduction of the hydrogen ion to  $H_2$  gas in the reactor, before the titrimetric measurements were made. More than 99% of the acid formed was collected in the reactor; the remainder being trapped in a downstream glass wool filter and cold trap.

#### Other Tests

In two tests we examined the effect of  $NO_x$  on  $SO_2$  conversion. The reactor was first operated with no  $NO_x$ ; in the second test we added 50 ppm  $NO$ , and in the third 50 ppm  $NO_2$ . In the latter two cases there was no observable difference in the amount of  $SO_2$  removed. Finally, we insulated all but one inch of the nichrome wire at the entrance with a teflon sleeve. The  $SO_2$  conversion was decreased by 90%, indicating that the activation process occurs all along the wire cathode.

#### DISCUSSION

Since the rate of disappearance of  $SO_2$  as  $H_2SO_4$  appeared to coincide with the formation of ozone (Figure 6) it seemed that the rate

determining step in the oxidation of  $\text{SO}_2$  was the ozone generation step.

Figure 12 is a plot of

$$\frac{\Delta \text{SO}_2}{(\text{SO}_2)_0} \text{ vs. } \frac{\text{O}_3}{(\text{SO}_2)_0}$$

for various initial  $(\text{SO}_2)_0$  values and residence times. The  $\text{O}_3$  values were taken from Figure 6 for the  $\Delta \text{SO}_2$  values corresponding to the same residence times. It is evident that there is very nearly a stoichiometric ratio of moles of sulfur dioxide removed for every mole of ozone produced.

Filippov, et al. (1962, 1967) conducted an extensive kinetic study of the electrical synthesis of ozone under flow conditions, and proposed the following expression for  $\text{O}_3$  synthesis:

$$\frac{d[\text{O}_3]}{dt} = k_1 [\text{O}_2] - k_2 [\text{O}_3] \quad (2)$$

The ordinary laws of kinetics may be applied to the case of flow reactions in electrical discharges by replacing the independent time variable in Equation 2 by a kinetic power factor  $U/v$ , where  $U$  is the applied power, watts, and  $v$  is the linear velocity, cm/sec. Therefore, Equation 2 may be solved for the case of excess  $\text{O}_2$ :

$$[\text{O}_3] = \frac{k_1 [\text{O}_2]}{k_2} \{1 - \exp(-k_2 U/v)\} \quad (3)$$

The above equation was fitted to the data presented in Figure 6 with the result that our data was represented quite well by such an expression with

$$k_1 \text{O}_2 = 11.55 \text{ ppm sec}^{-1} = 52.1 \text{ ppm cm (watt sec)}^{-1}$$

$$k_2 = 0.0154 \text{ sec}^{-1} = 0.0695 \text{ cm (watt sec)}^{-1}$$



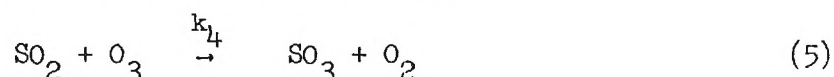
We considered several possibilities for the mechanism of  $\text{SO}_2$  removal. Gerh rd and Johnstone (1955) investigated the photochemical oxidation of  $\text{SO}_2$  by sunlight. They found a first order relationship

$$\frac{d [\text{SO}_2]}{dt} = -k_3 [\text{SO}_2] \quad (4)$$

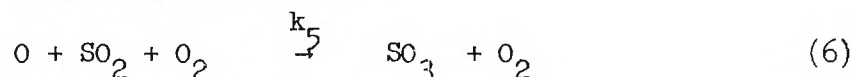
where  $k_3 = 1.6 \times 10^{-6} \text{ sec}^{-1}$ .

This rate is about  $10^4$  slower than what we experienced with the corona discharge reactor. Also there seems to be no means of accounting for the loss of ozone on this route.

Powers and Cadle (1965) tested the reaction



with concentrations 1 - 10%  $\text{SO}_2$ , 1%  $\text{O}_3$  and 1% water vapor and found that less than 0.1% of the  $\text{SO}_2$  had reacted in a 24 hour period. This work was confirmed by Dunham (1960) who found no significant condensation nuclei of  $\text{H}_2\text{SO}_4$  from the  $\text{SO}_2 - \text{O}_3$  reaction. Mulcahy, et al. (1967) studied the kinetics of reactions between atomic oxygen and sulfur dioxide. Their work showed that the kinetics of the  $\text{SO}_2$  conversion can be explained by the termolecular combination reaction:



where

$$K_5 = 5.4 \times 10^{-6} (\text{ppm})^2 \text{ sec}^{-1}$$

If we take  $[\text{O}] \approx [\text{O}_3]$ , then at equilibrium

$$[\text{O}] \approx [\text{O}_3] = \frac{k_1 [\text{O}_2]}{k_2} \quad (7)$$

so an estimate can be made of the rate of formation of  $\text{SO}_3$ :

$$\frac{d[\text{SO}_3]}{dt} = k_5 [\text{SO}_2][\text{O}_2] \frac{k_1 [\text{O}_2]}{k_2} \quad (8)$$

and this can be compared with the maximum rate of formation of  $\text{O}_3$

$$\frac{d[\text{O}_3]}{dt}_{\text{max}} = k_1 [\text{O}_2] \quad (9)$$

$$\begin{aligned} \frac{\frac{d[\text{SO}_3]}{dt}}{\frac{d[\text{O}_3]}{dt}_{\text{max}}} &= \frac{k_5 [\text{SO}_2][\text{O}_2]}{k_2} \\ &= 7.4 \times 10^4 \gg 1 \end{aligned} \quad (10)$$

Therefore even though the  $[\text{O}_2] / [\text{SO}_2]$  relative concentration is on the order of 20/1 the relatively high rate constant in Equation 6 favors the formation of  $\text{SO}_3$  and the  $\text{O}_3$  will be formed in negligible amounts.

Injection of oxides of nitrogen showed no effect on reaction rates, however, the concentrations used (50 ppm) may have been inappropriate. Wilson et al. (1970) observed that  $\text{SO}_2$  is removed by a product of the reaction of  $\text{NO}_2$  and  $\text{O}_3$ . They suggested that  $\text{NO}_3$  or  $\text{N}_2\text{O}_5$  reacts with  $\text{SO}_2$  to form  $\text{SO}_3$  and  $\text{NO}_2$ . Gerhard and Johnstone (1955) reacted 1 to 2 ppm of  $\text{NO}_2$  with 10 to 20 ppm  $\text{SO}_2$  in irradiated light (2950-2650 Å) and found no measurable effect. However, Renzetti and Doyle's experiments (1960) showed that the addition of 1 ppm  $\text{NO}_2$  to 0.14 ppm  $\text{SO}_2$  enhanced the photooxidation of  $\text{SO}_2$ . Further experiments at higher  $\text{NO}_2$  concentrations

will reveal whether this enhancement effect can be duplicated in the case of corona discharge stimulated reactions.

The nucleation process was not studied in this work, but since air humidified by a bubbling process contains water nuclei and since the metal wire cathode is continuously ejecting metal particles, the presence of condensation nuclei may enhance the overall rate of droplet formation and ultimate size of the deposited droplets. This is not expected to be a rate limiting step, however, since  $\text{SO}_3$  is strongly self nucleating in the presence of water vapor, and proceeds at rates far greater than the  $\text{SO}_2$  oxidation step.

#### CONCLUSIONS

The rate of oxidation of sulfur dioxide in humid air in the presence of a corona discharge is zero order with respect to  $\text{SO}_2$  in the range 500-3000 ppm. The reaction was strongly dependent on oxygen and the oxidation rate diminished for  $\text{O}_2$  concentrations below 14 percent. By measuring the rate of ozone formation in the absence and presence of  $\text{SO}_2$ , it appears that the rate controlling mechanism for the  $\text{SO}_2$  oxidation lies in the break-down of the oxygen molecule by the corona discharge to form atomic oxygen. Apparently the  $\text{SO}_2$ -O reaction is several orders of magnitude faster than the  $\text{O}_2$ -O reaction. About 75 percent of the  $\text{SO}_2$  removed precipitated in the form of sulfuric acid mist on the wall of the reactor. Studies of the precipitated droplets indicate a mean size of  $6.36\mu$  before deposition. Deposition patterns were consistent for the entire length of the reactor suggesting that aerosol movement was almost exclusively in the radial direction. Oxides of nitrogen at 50 ppm showed no measurable effect on the sulfur dioxide reaction rate.

# LITERATURE CITED










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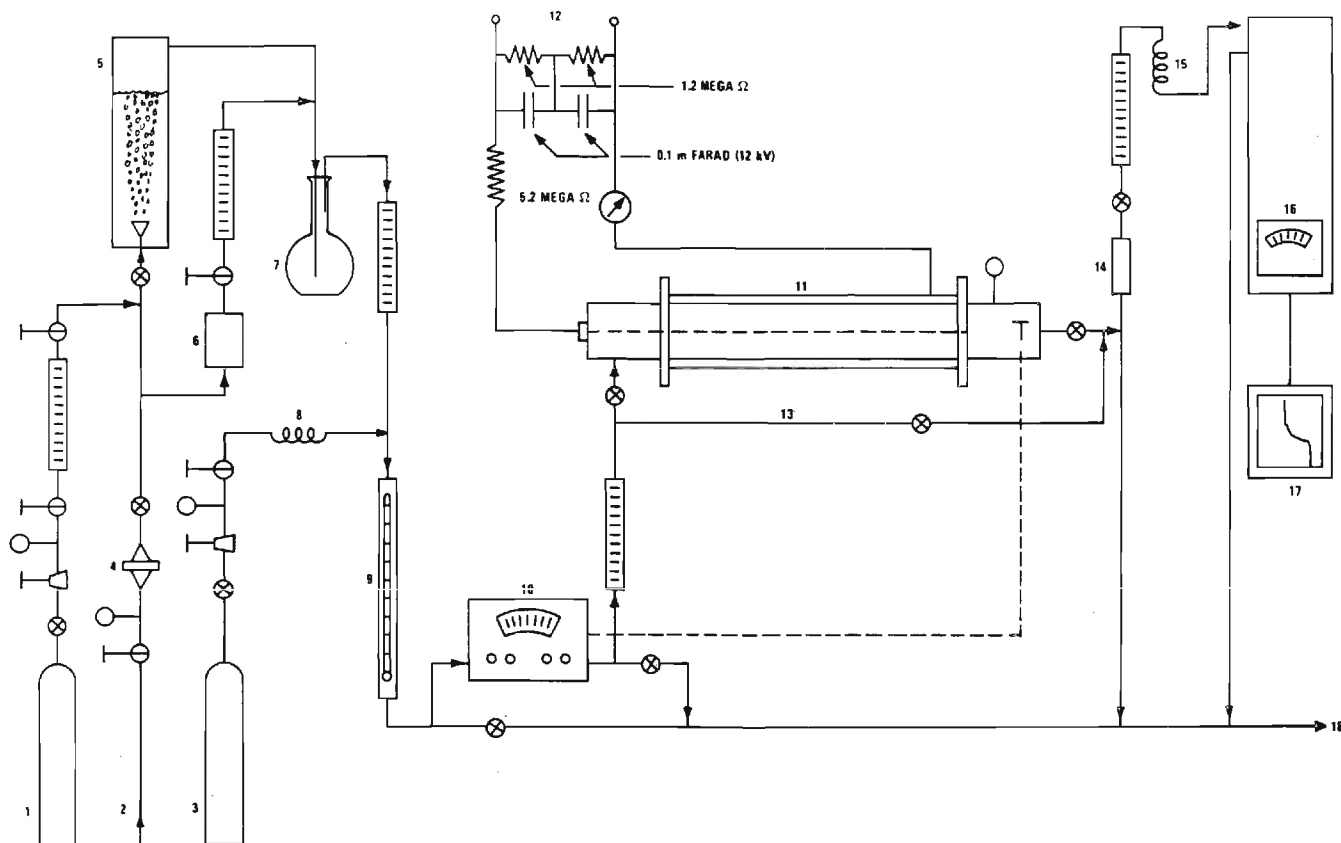


- Figure 1. Experimental Arrangement
- Figure 2. Corona Discharge Reactor
- Figure 3. Initial removal rates for various  $\text{SO}_2$  concentrations.
- Figure 4. Fraction of sulfur dioxide removed as a function of relative humidity of the carrier air stream. Vertical lines represent spread in data; 1.0 l/min flow rate at 1000 ppm  $\text{SO}_2$  initial concn.
- Figure 5. Influence of oxygen concentration on sulfur dioxide removal, 5.0 l/min gas flow rate at 1000 ppm  $\text{SO}_2$  initial concn.
- Figure 6. Ozone generation rates without  $\text{SO}_2$ ,  $\bigcirc$ ; with 1000 ppm  $\text{SO}_2$ ,  $\bullet$ ;  $\text{SO}_2$  removal rate  $\Delta$ , for 1000 ppm initial concentration.
- Figure 7. Effect of applied power on  $\text{SO}_2$  removal for various flow rates, 0.5 l/min,  $\bigcirc$ ; 1.0 l/min,  $\Delta$ ; 3.0 l/min,  $\square$ . Initial  $\text{SO}_2$  concentration, 1000 ppm and 70 percent RH.
- Figure 8. Power consumption per SCF vs. operation time. Flow rate, 0.5 l/min; 1000 ppm  $\text{SO}_2$ , 70% relative humidity.
- Figure 9. Cumulative particle size distribution for acid droplets impacted on reactor wall.
- Figure 10. Fraction of sulfur dioxide removed vs. moles of ozone generated during the same residence time. Solid line represents  $\Delta(\text{SO}_2) = (\text{O}_3)$ ; dashed line is least squares fit. Residence times - 2.5 min,  $\Delta$ ; 1.92 min,  $\bigcirc$ ; 1.25 min,  $\blacktriangle$ ; 0.63 min,  $\square$ ; 0.42 min,  $\bullet$ ; 0.32 min,  $\blacksquare$ .

- 1 - N<sub>2</sub> CYLINDER
- 2 - COMPRESSED AIR
- 3 - SO<sub>2</sub> CYLINDER
- 4 - MILLIPORE FILTER
- 5 - HUMIDIFIER COLUMN
- 6 - DRYING TUBE (SILICA GEL)
- 7 - CONDENSATE TRAP/MIXING CHAMBER
- 8 - HIGH PRESSURE DROP CAPILLARY COIL
- 9 - TOTAL IMMERSION THERMOMETER
- 10 - DEW POINT HYDROMETER
- 11 - CORDNA REACTOR
- 12 - POWER SUPPLY
- 13 - BYPASS LINE
- 14 - GLASS-WOOL FILTER
- 15 - FREEZE-OUT TRAP
- 16 - SO<sub>2</sub> INFRARED ANALYZER
- 17 - STRIP CHART RECORDER
- 18 - DRAIN

# SYMBOLS:

-  VALVE
-  PRESSURE REGULATOR
-  PRESSURE INDICATOR
-  NEEDLE VALVE
-  ROTAMETER
-  THERMISTOR
-  AMMETER
-  RESISTOR
-  CAPACITOR



- |  |                                    |
|--|------------------------------------|
| ① 1/8" SS ROD (6" LENGTH)  | ⑥ 2" I. D. PLEXIGLAS TUBE          |
| ② ELECTRICAL CONNECTOR   | ⑦ "O" - RING                       |
| ③ 1" THREADED S.S. TUBE  | ⑧ 6" X 6" TEFLON END PLATES        |
| ④ STD 1/4" BOLT (SEE INSERT)   | ⑨ 2" I. D. S.S. TUBE               |
| ⑤ 3 1/4" PLEXIGLAS FLANGE WITH<br>6 HOLES EQUALLY SPACED ON<br>2 3/4" B.C. FOR 6 STD 1/4" S.S. BOLTS | ⑩ 1/2" S.S. GROUND LUG             |
|  | ⑪ COAXIAL WIRE HOLDER (SEE INSERT) |

