THE EFFECT OF AN ELECTRICAL CORONA DISCHARGE UPON THE REACTION OF SO_2 TO SO_3 IN LOW CONCENTRATION SO_2 - AIR MIXTURES

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ABSTRACT

An investigation of a pilot plant electrical dust precipitator was conducted to determine its ozone generating characteristics in air as well as the ability of the ozone formed to convert gaseous SO_2 to particulate SO_3. It was anticipated that in addition to the known primary particulate dust and mist removal function of a precipitator, a secondary gaseous removal facility was inherent in its operation.

Ozone formation quantities were determined at varied air flow and electrical power input levels to the precipitator. Maximum ozone generation was 0.02 pounds per hour at an energy input level of 113 KW-HR per pound - approximately one-seventh the efficiency of commercial ozonators.

Conversion of gaseous SO_2 to particulate SO_3 by the ozone generated in the precipitator was determined at varied SO_2 concentration levels and air flow rates. Two definite reactions were observed in the formation of SO_3 from SO_2 by ozone. At SO_2 concentrations below 100 P.P.M. five mols of O_3 are required per mol of SO_3 formed whereas above SO_2 concentrations of 400 P.P.M. one mol of ozone produced three mols of SO_3.

An evaluation of the results obtained indicates that a commercial electrical dust precipitator is an impractical device for reducing gaseous SO_2 by reaction of generated ozone to form particulate SO_3. While 100% of the generated ozone can convert gaseous SO_2 to particulate SO_3, the SO_2 concentration levels required for the reaction are such that less than 1% of the total SO_2 is removed from the gas stream.

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TABLE OF CONTENTS

PAGE

PAGE

LIST OF FIGURES

FIGURE

LIST OF TABLES

TABLE

INTRODUCTION

In the commercial utilization of Cottrell electrical precipitators for the removal of suspended solids and mists from industrial waste gases, high voltage electrical fields with their associated high intensity "corona" discharges are employed as the basic particle charging and collecting forces to separate the suspensoids from the gas streams. These high intensity electrical forces and fields are analogous to those utilized in commercial electrical ozonators for the synthesis of ozone from air or oxygen. As these two processes are inherently similar, an investigation was conducted on a pilot type Cottrell electrical precipitator in order to compare its ozone generating characteristics with those of modern highly efficient commercial ozone generators.

In addition to solid particulates, industrial waste gases often contain objectionable gaseous components such as SO_2, which should also be removed prior to the ultimate discharge of the waste gases to the atmosphere. If the negative "corona" discharges in a Cottrell precipitator generate ozone, this can react with gaseous SO_2 to form SO_3. The SO_3 thus created, in the presence of water vapor, would form particulate sulphuric acid mist and in turn be collected in a precipitator as a secondary product along with the native solid dust and mist particles.

The subject investigation, after ozone generating characteristics were determined in the pilot precipitator, was therefore extended to evaluate the effects of the reaction of ozone upon SO_2 within the installation.

The overall pilot plant results obtained were then extrapolated to a commercial size precipitator in order to evaluate the feasibility of the overall process on an industrial scale.

GENERAL THEORY

Ozone Generation in an Electrical Discharge

The formation of ozone from oxygen requires the absorbtion of energy equivalent to 34 K cal. per gram-mol of ozone formed.

$$68 \text{ K cal.} + 3O_2 \dashrightarrow 2O_3 \text{ or } \Delta H = +34 \text{ K cal./mol. } O_3$$

The most efficient method of commercially producing ozone to date has been through the electrical gaseous discharge. In this process oxygen molecules are dissociated into oxygen atoms by inelastic collisions with high energy electrons generated by the electrical discharge.

$$59 \text{ K cal.} + e^{-1} + O_2 = e^{-1} + O + O \text{ or } \Delta H = +59 \text{ K cal./mol. } O_2$$

The oxygen atoms thus formed react with undissociated oxygen molecules to form ozone with the liberation of heat.

$$O + O_2 = O_3 + 24.6 \text{ K cal. or } \Delta H = -24.6 \text{ K cal./mol. } O_3$$

The minimum reaction starting energy required for the dissociation of the oxygen molecule in an electrical discharge is therefore 118 K cal. per gram-mol of ozone formed. (5.11 electron volts). This is well above the 34 K cal./mol. requirement of the heat of formation - however, it is necessary in order to electrically dissociate the oxygen molecule to atomic oxygen for the subsequent reaction with oxygen to form ozone.

The following summarizes the minimum energy considerations for ozone generation by this electrical discharge process.

(Electron Bombardment of Oxygen Molecule)

$$2O_2 + O_2 + 2e^{-1} = 2O_2 + 2e^{-1} + O + O \text{ (118 K cal./mol. } O_3 \text{ required)}$$

(Reaction of Active Oxygen with Normal Oxygen)

$$2O_2 + 2e^{-1} + O + O = 2O_3 + 2e^{-1} \text{ (24.6 K cal./mol. } O_3 \text{ liberated)}$$

(Overall Reaction)

$$3O_2 + 2e^{-1} = 2O_3 + 2e^{-1} \text{ (142.6 K cal. available/mol. } O_3 \text{ formed)}$$

In the most favorable ozonators to date total energy requirements for production are in the order of 410 K cal./mol. ozone formed or approzimately 12 times the energy equivalent of the heat of reaction. A more average value for standard commercial ozonators utilizing air is approximately 760 K cal./mol. ozone or 22.5 times the theoretical heat of reaction.

Reaction of Ozone with SO_2

Sulphur dioxide can potentially be oxidized by ozone to sulphur trioxide. The overall reaction for this is generally represented as follows:

$$3SO_2 + O_3 = 3SO_3 \qquad \Delta H = -105.13 \text{ K cal./mol. } O_3$$

Significant literature on this reaction is scant and conflicting with yields reportedly varying from 0 to 100%. The most recent work evaluated (2) indicated that O_3 yields (% O_3 which is utilized) varied directly with the initial ozone to sulphur dioxide concentrations for molar ratios of 0.4 to 2.2. At equal molar concentrations, yields were approximately 33%. This data was obtained in the temperature range of 85 to 235°C with reaction times varying from 3 to 120 seconds. It was reported that the findings qualitatively agreed with the reversible decomposition of ozone into molecular and atomic oxygen according to the Jahn mechanism for ozone decomposition. Approximately two-thirds of the atomic oxygen thus formed further decomposed additional ozone to oxygen. The remaining atomic oxygen reacted with SO_2 to form SO_3.

$$O_3 \rightleftarrows O_2 + O$$

$$O + O_3 \longrightarrow 2O_2$$

$$O + SO_2 \longrightarrow SO_3$$

Temperature was indicated to have little effect upon yields within the ranges evaluated and water vapor was of secondary importance.

If this hypothesis be valid, then the following theoretical reactions occur in the formation of of $S0_3$ from $S0_2$ by ozone:

$$\begin{array}{lllll} & & 0 + S0_2 & \dashrightarrow & S0_3 \\ S0_2 + 30_3 \dashrightarrow & 30_2 \dashrightarrow & 0 + 0_3 & \dashrightarrow & 20_2 \\ & & 0 + 0_3 & \dashrightarrow & 20_2 \end{array}$$

or

$$S0_2 + 50_3 \dashrightarrow 70_2 + S0_3$$

This is an expenditure of 5 mols. of ozone for every mol. of SO_2 reacted and mol. of SO_3 produced. On the other hand, if the general reaction occurs, $3SO_2 + O_3 = 3SO_3$, then 1 mol. of ozone will react with 3 mol. of SO_2 to form 3 mols. of SO_3. This is a 15 to 1 difference in SO_3 production or ozone utilization, hence it was considered necessary to determine the actual generation conditions within the pilot precipitator.

SCOPE OF THE EXPERIMENT

The experiment was broadly divided into two phases, namely; tests on the pilot electrical precipitator and the calibration of same for ozone generation rates, then the sulphur oxide conversion tests.

Phase 1

Ozone generation. Ozone generation rates in ambient plant air by a pilot electrical precipitator operated at varied power input levels and air flow rates were established during this phase of the experiment. The following data were tabulated for each test run.

1. Inlet and outlet air temperatures to the precipitator.
2. Electrical power input to the precipitator, specifically secondary voltages and currents.
3. Ozone concentrations of the air leaving the precipitator in parts per million by volume.
4. Air flow rates through the precipitator.

The above data, after analysis, formed the basis of calibration of the electrical precipitator as an ozonator. Curves were developed to indicate the quantity of ozone generated from ambient air at any given air flow rate and power input level within the design range of the equipment. This information was subsequently utilized to predict the ozone concentration levels generated electrically during the sulphur oxide conversion tests.

Phase 2 - Sulphur Oxide Conversion Tests

SO_2 Injection. An SO_2 gas injection station was established and preliminary calibration tests were performed to provide a primary regulation of the SO_2 injection system. Final measurements, after primary regulation of the SO_2 injection rates, were obtained by precipitator inlet analysis of the varied SO_2 - air mixtures during the actual SO_3 conversion test periods. The minimum SO_2 in air concentration levels which could be reliably and continuously maintained was approximately 100 p.p.m. SO_2 by volume at a maximum air flow rate of approximately 340 ACFM. This established the minimum operating SO_2 level of the system for the SO_3 formation tests.

SO_3 formation tests. Outlet SO_3 formation quantities were measured at two air flow rates with varied SO_2 - air concentrations and varied electrical power inputs to the precipitator. Performance curves were then established to allow prediction of the levels of SO_3 formation under the varied operating conditions of the precipitator.

Conversion efficiencies. The above data, after analysis, provided the final basis for establishing the conversion efficiency of the reactor in creating SO_3 from SO_2 in air by means of an electrical corona discharge. Conversion efficiency was evaluated on the basis that complete or 100% conversion was the equivalent of complete reaction of all the ozone created with sulphur dioxide in the gaseous state to form sulphur trioxide at temperatures below 115°F.

DESCRIPTION OF TEST ARRANGEMENT AND EQUIPMENT

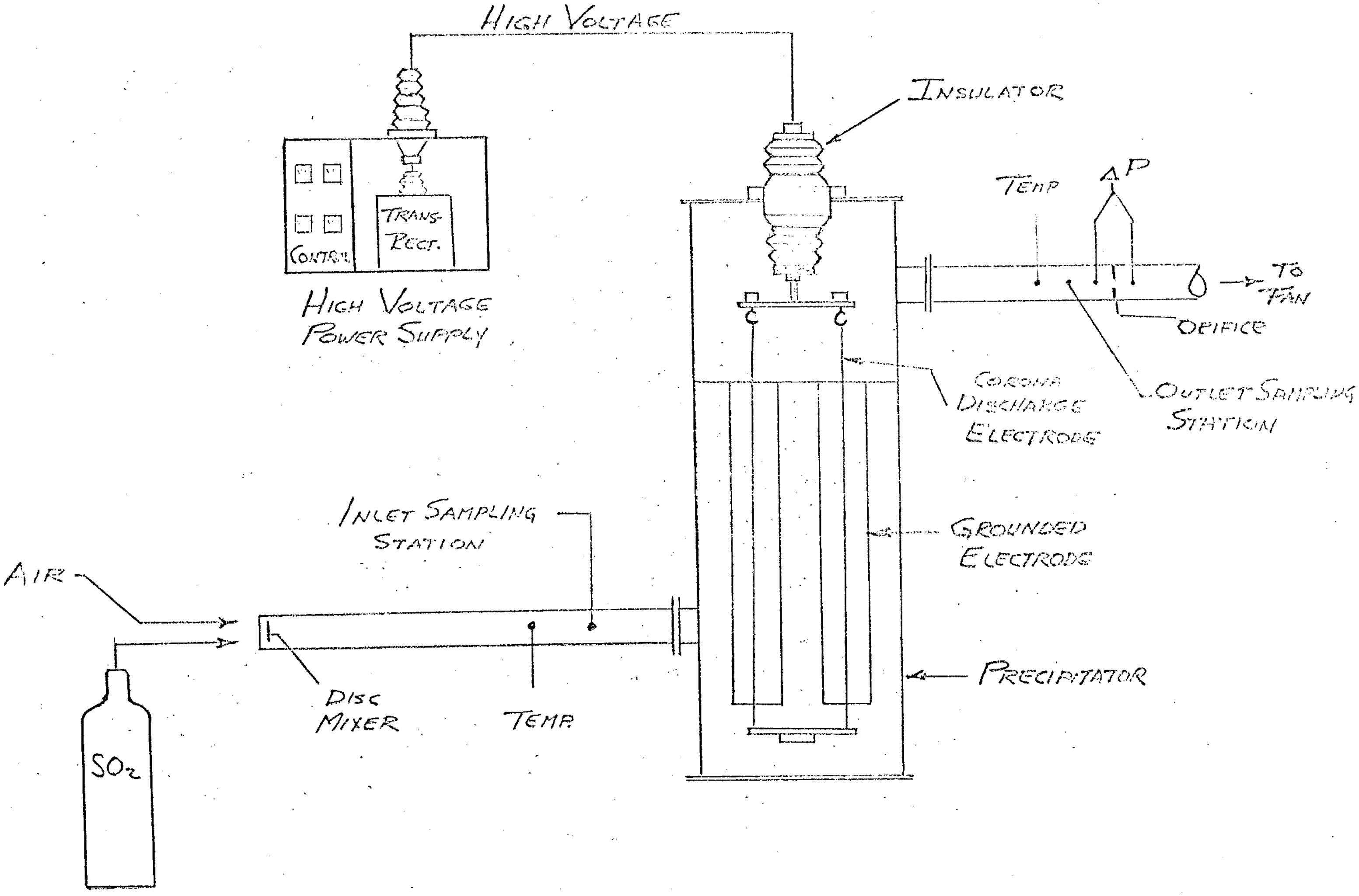
Ozone Generator

A pilot type electrostatic precipitator was utilized as the ozone generating reactor. This installation was constructed of mild steel and contained four parallel grounded pipe type electrodes each 3'' dia. x 3'-6'' long. Attached at the bottom of these electrodes was a hopper type gas inlet plenum chamber, and affixed to the top was a combination outlet plenum chamber and high voltage inlet bushing housing.

Suspended concentrically within each grounded pipe electrode was a 50 mil diameter steel high voltage discharge electrode (total of four). These were attached in the top chamber through a grid support to an electrically insulated high voltage, lead-in, support bushing. Each discharge electrode was held taunt and centered within its associated pipe by means of a cast iron weight attached to the bottom of the electrode.

High Voltage Connection Cable

A dry type high voltage electrical cable was installed to connect the reactor high voltage discharge electrode system to the secondary side of the high voltage transformer-rectifier power supply.



GENERAL ARRANGEMENT OF TEST EQUIPMENT

FIGURE No 1.

Transformer Rectifier

An oil immersed 15 KVA transformer and a four tube, full-wave, bridge type vacuum tube rectifier was used to step up and rectify a 440 volt, 1 phase, 60 cycle primary power supply to full-wave voltages of 50 K.V. maximum and maximum D.C. currents of 230 milliamperes.

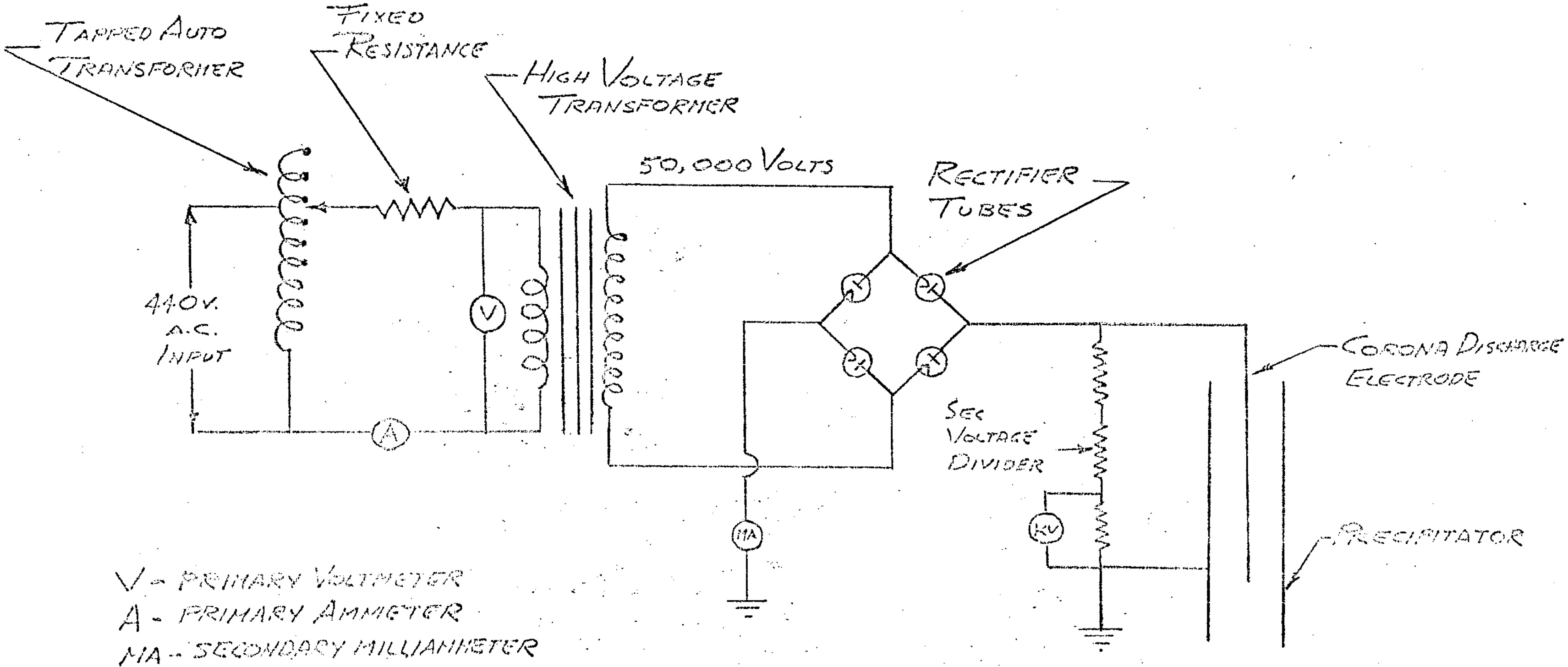
Transformer Rectifier Control System

A tapped auto transformer was included in the transformer control circuit to allow for variation in the output power supplied to the pilot precipitator or reactor. A 2.5 ohm fixed resistance was installed in the transformer primary circuit for overload protection during reactor "spark-over" periods. Primary transformer voltages and currents were measured by standard control meters whereas secondary voltages were measured across a 200,000 ohm resistor on the high voltage side of the rectifier. Secondary reactor currents were measured by a milliampere meter located in the ground return leg of the high voltage system.

Figure No. 1 indicates the general arrangement of the electrostatic precipitator, whereas Figure No. 2 outlines the electrical arrangement of the transformer-rectifier and control system.

Flue Layout

Figure No. 1 also includes an outline of the overall system



V - PRIMARY VOLTMETER
A - PRIMARY AMMETER
MA - SECONDARY MILLIAMMETER
KV - SECONDARY VOLTMETER

SCHEMATIC DIAGRAM OF ELECTRICAL EQUIPMENT

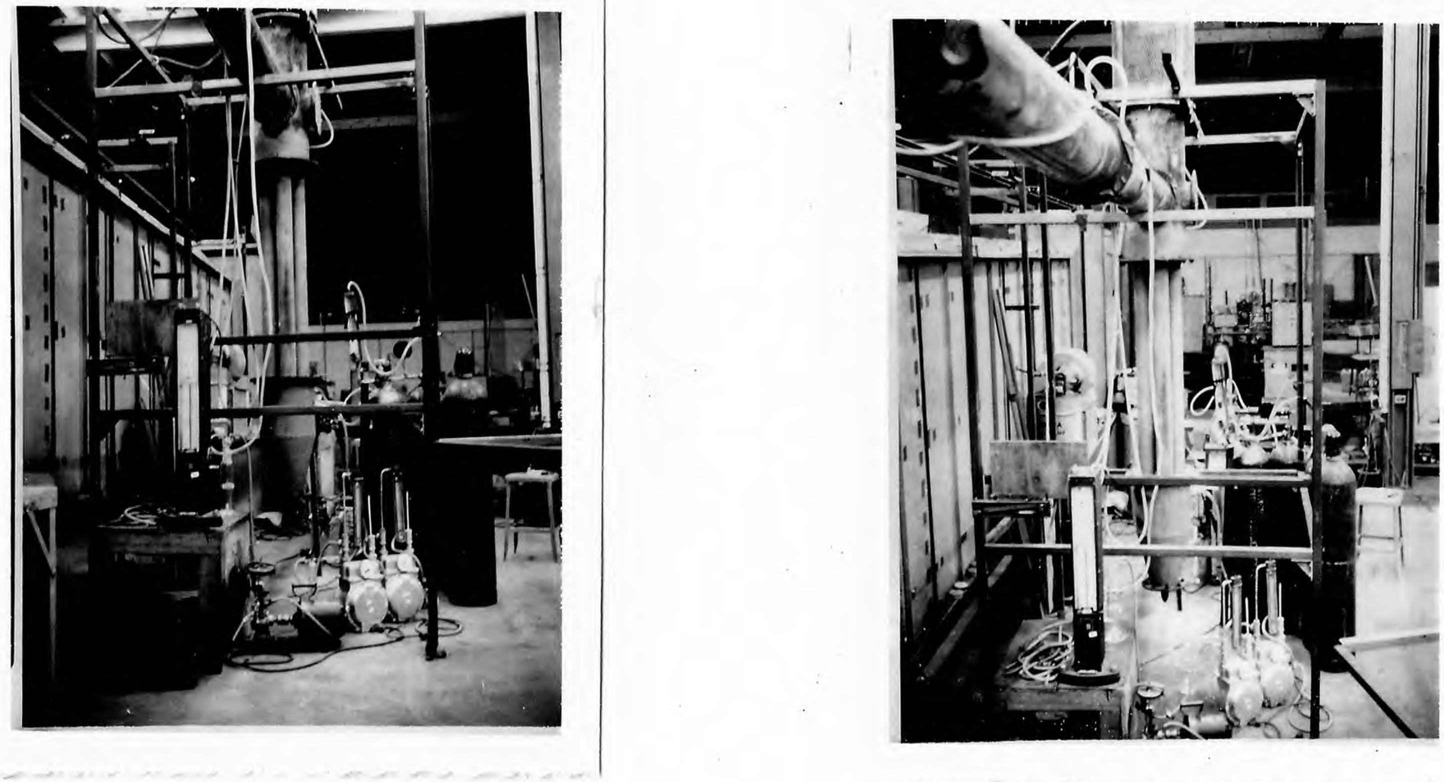
FIGURE Nº 2

arrangement. Basically a 4" dia. steel pipe was equipped at its inlet end with a disc type gas mixer. SO_2 gas was injected from a pressurized cylinder, through the disc mixer then the mixed air/SO_2 gas was passed through the 4" inlet pipe to the ozone generator-reactor. Upon leaving the reactor the gases then passed through an 8" dia. steel flue equipped with a 4.25" dia. sharp edged orifice, then were drawn through an I.D. fan equipped with a flow regulating slide gate damper and exhausted to the atmosphere. Located between the orifice and fan inlet was a secondary air bleed-in damper which allowed for fine adjustment of the gas or air flow through the system.

Sampling Test Stations and Equipment

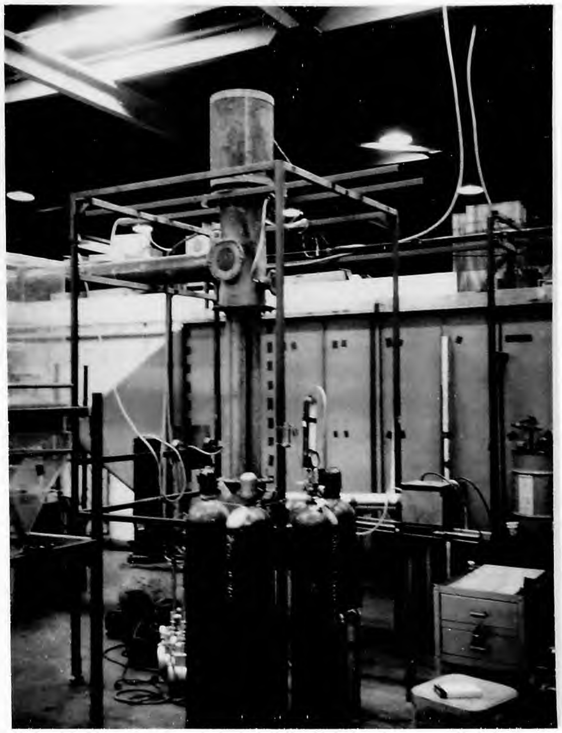
Gas sampling connections were located immediately before the reactor inlet flange and six pipe diameters downstream from the reactor outlet flange. Tygon tubing was used to pass the sampled gases between the test connections and the glass absorbtion bottles while rubber tubing was used between the abosrbtion bottles and the dry gas sampling meters. Dry type gas meters equipped with mercury manometers, thermometers and volumetric dials were used to record the conditions and rate of gas sampling. Motor driven vacuum pumps located after the gas meters were used to aspirate the sampled gases from the flues through the sampling system.

Photographs of the entire test arrangement and equipment are indicated on Figures No. 3, 4, and 5.



Views of Ozone Generator Flues and Sampling Equipment

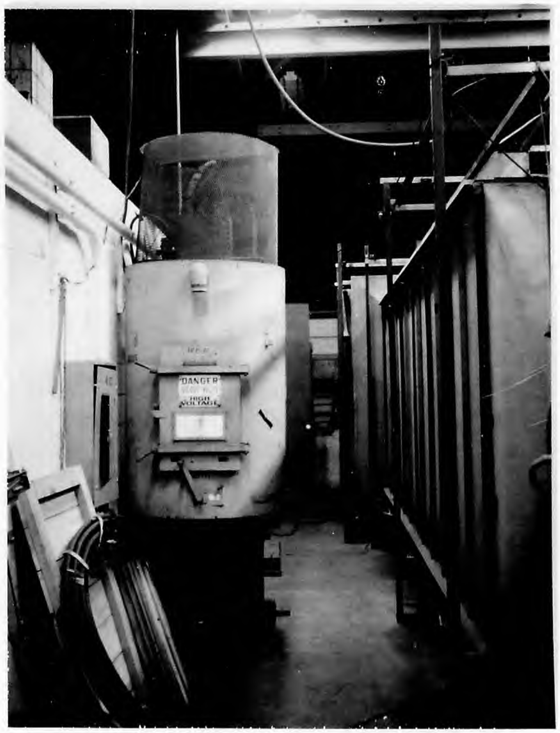
Figure No. 3



View of SO_2 Generation Station and Precipitator

View of Chemical Analysis Lab

Figure No. 4



View of High Voltage
Transformer-Rectifier

View of Transformer-Rectifier
Control Panel and Meters

Figure No. 5

TEST PROCEDURE AND TECHNIQUES

Orifice Calibration - Air Flow Measurements

A 4.25" diameter sharp-edged orifice was located in the 8" dia. flue between the reactor outlet and fan inlet. Static pressure taps were located 1 1/2 pipe diameters upstream and downstream from the orifice plate and connected to a water manometer sensitive to .001" H_2O pressure differential. Pitot tube traverses were obtained at four fan damper settings corresponding to air flow rates of 145, 225, 320 and 360 cfm air. From these four points and their corresponding manometer pressure differentials a calibrated orifice air flow rate curve was developed. This is as indicated on Figure #6. All subsequent air flow rates were established from this curve in conjunction with orifice manometer readings recorded during the various tests.

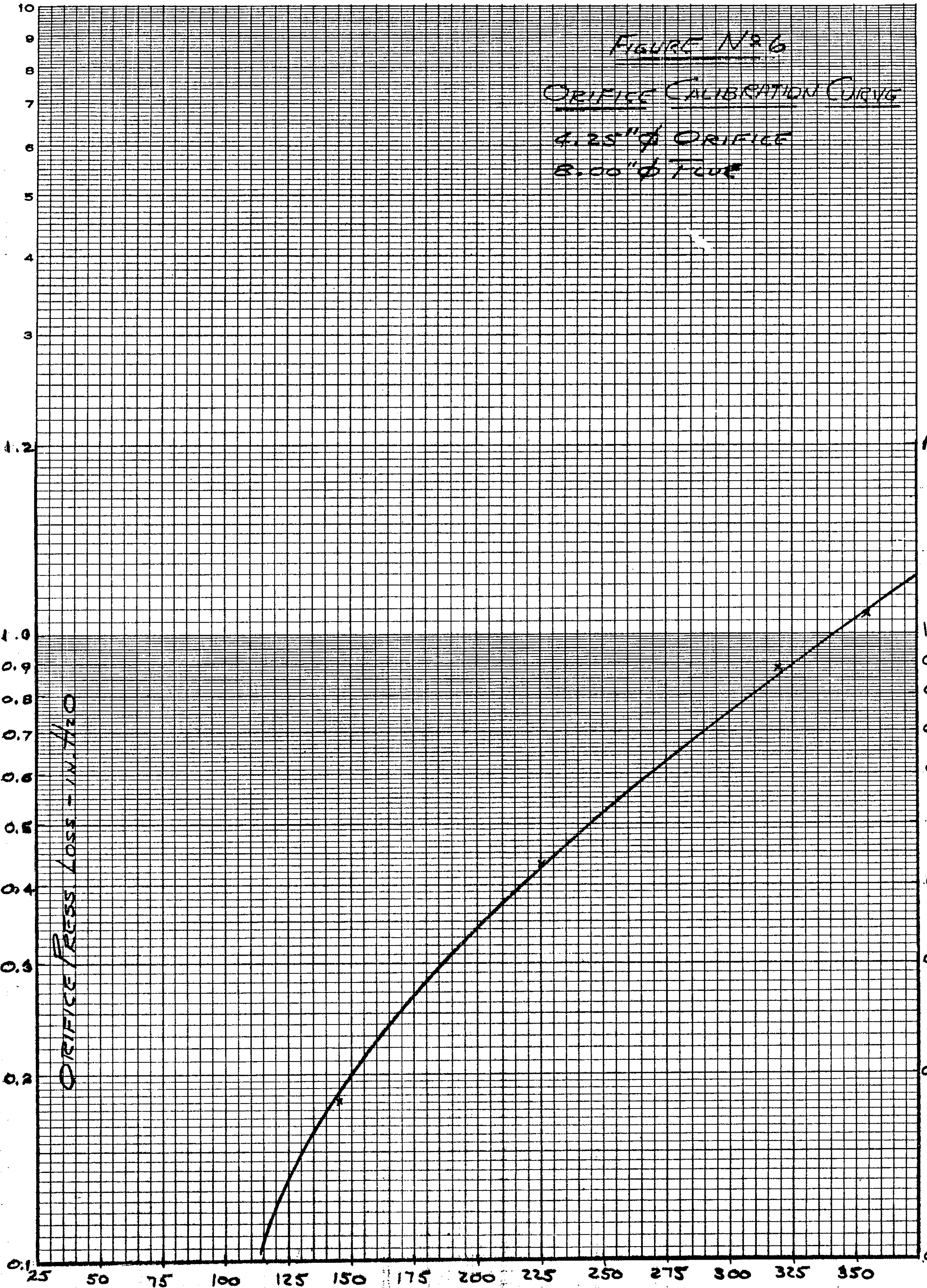


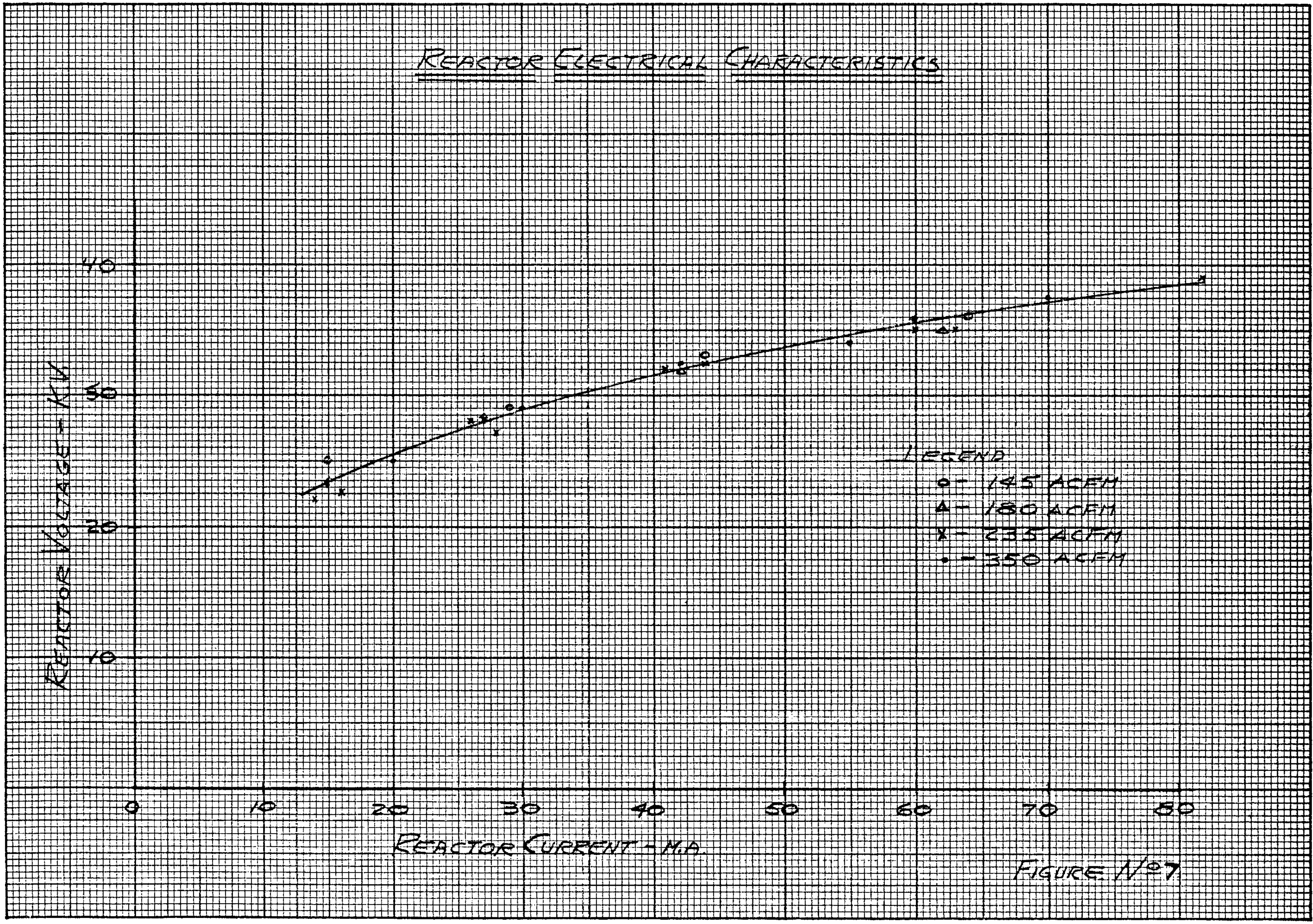
FIGURE No 6

ORIFICE CALIBRATION CURVE

4.25" Ø ORIFICE
8.00" Ø FLUE

Reactor Electrical Characteristics and Measurements

Transformer, hence reactor secondary voltages and currents, were obtained by measurements of a rectified 440 volt, single phase, 60 cycle primary supply. A kilovoltmeter and a milliampere current meter, in conjunction with an oscilloscope, were utilized to record the full-wave secondary electrical readings at varied transformer tap settings. Within the range of air flow rates utilized, the secondary voltages and currents were reasonably constant. Figure No. 7 is a plot of the reactor full-wave voltage current relationships up to the "spark-over" or electrical break down limit of the reactor for the ranges of air flow rates investigated. Maximum power input level before electrical "spark-over" is normally 2400 watts corresponding to 36 KV at 63 milliamps. Minimum power input level was approximately 24 KV @ 14 milliamps corresponding to 335 watts.



REACTOR ELECTRICAL CHARACTERISTICS

FIGURE No 7

Ozone Generation Rates

Ozone generation rates were determined by sampling a portion of the reactor exhaust air while concurrently measuring the electrical power input, the rate of gas flow, and inlet and outlet air temperatures of the reactor. The reactor outlet samples were drawn, at a rate of 0.3 to 0.4 C.F.M. for ten minute periods, through an absorption bubbler containing 250 ml. of 0.1 N potassium iodine solution. At the conclusion of each ten minute test, the total metered air sample was converted to standard conditions (32°F & 29.92" Hg.). In addition, the quantity of iodine liberated in the bubbler was determined by titration with a .002 N sodium thiosulphate solution. The quantity of ozone generated for a specific test was then calculated (P.P.M. by volume) by the following relationship:

$$O_3 = \frac{0.79\ (\text{ml. } 0.1\text{ N } Na_2S_2O_3)}{\text{std. cu. ft. air sampled}} = \frac{0.79\ (\text{ml.})}{\text{S.C.F.}}$$

A total of thirty-five (35) test runs were obtained basically at four gas flow rates with varied electrical power inputs. The results of all these tests are summarized in Table No. 1

Figure No. 8 is a plot of the ozone generation rates obtained (p.p.m. by vol.) as a function of the reactor current input (milliamperes) for all thirty-five tests. An analysis of the above data

TABLE 1. SUMMARY OF OZONE GENERATION TESTS

		Orifice P	Air Flow	Air Temp. °F		Elec. Rdgs.		Ozone
Date	Run	("H2O)	(ACFM)	In	Out	KV	ma	(PPM)
9/11/64	#1	1.06	350	76	86	29	30	4.02
	#2	1.06	350	76	86	29	30	3.75
	#3	1.06	350	76	81	25	20	2.63
	#4	1.06	350	76	81	25	20	2.63
	#5	1.06	350	76	94	34	55	6.55
	#6	1.06	350	76	94	34	55	6.22
	#7	1.06	350	76	102	37.5	70	8.12
	#8	1.06	350	76	102	37.5	70	7.85
9/18/64	#9	0.43	225	71	75	24	14	2.6
	#10	0.43	225	71	75	24	14	2.6
	#11	0.43	225	72	80	28	26	3.9
	#12	0.43	225	72	80	28	26	4.1
	#13	0.43	225	71	88	32	41	5.75
	#14	0.43	225	71	99	35	60	7.6
	#15	0.43	225	71	112	39	82	9.3
9/19/64	#16	0.170	145	71	78	25	15	3.5
	#17	0.170	145	71	86	29	28	6.56
	#18	0.170	145	72	98	33	44	10.7
	#19	0.170	145	72	114	36	64	14.3
9/26/64	#20	0.256	180	74	108	35	62	12.0
	#21	0.256	180	74	97	32	42	8.8
	#22	0.256	180	75	88	28	27	5.6
	#23	0.256	180	75	82	23	15	3.03
9/27/64	#25	0.990	335	76	97	36	60	7.1
	#26	0.990	335	77	90	32.5	42	5.6
	#27	0.990	335	77	85	28	27	3.46
	#28	0.990	335	77	81	23	15	1.80
	#29	0.433	225	77	95	32	42	6.4
	#30	0.433	225	78	107	36	61	8.9
1/3/65	#31	0.508	245	73	99	35	63	8.9
	#32	0.508	245	73	91	32.5	44	7.3
	#33	0.508	245	73	84	27	28	5.0
	#34	0.508	245	73	78	22.5	16	2.88
	#35	0.508	245	73	99	35	63	9.5

has indicated the following general relationship between rate of ozone generation and current input for the particular reactor design used in this test program.

$$O_3 = 37 \frac{I}{V}$$

where O_3 = Ozone generated (p.p.m. by volume)

I = Reactor secondary current flow (ma)

V = Air flow through the reactor (A.C.F.M.)

In all subsequent tests and calculations the ozone generated was determined from Figure No. 8.

OZONE GENERATION CURVE

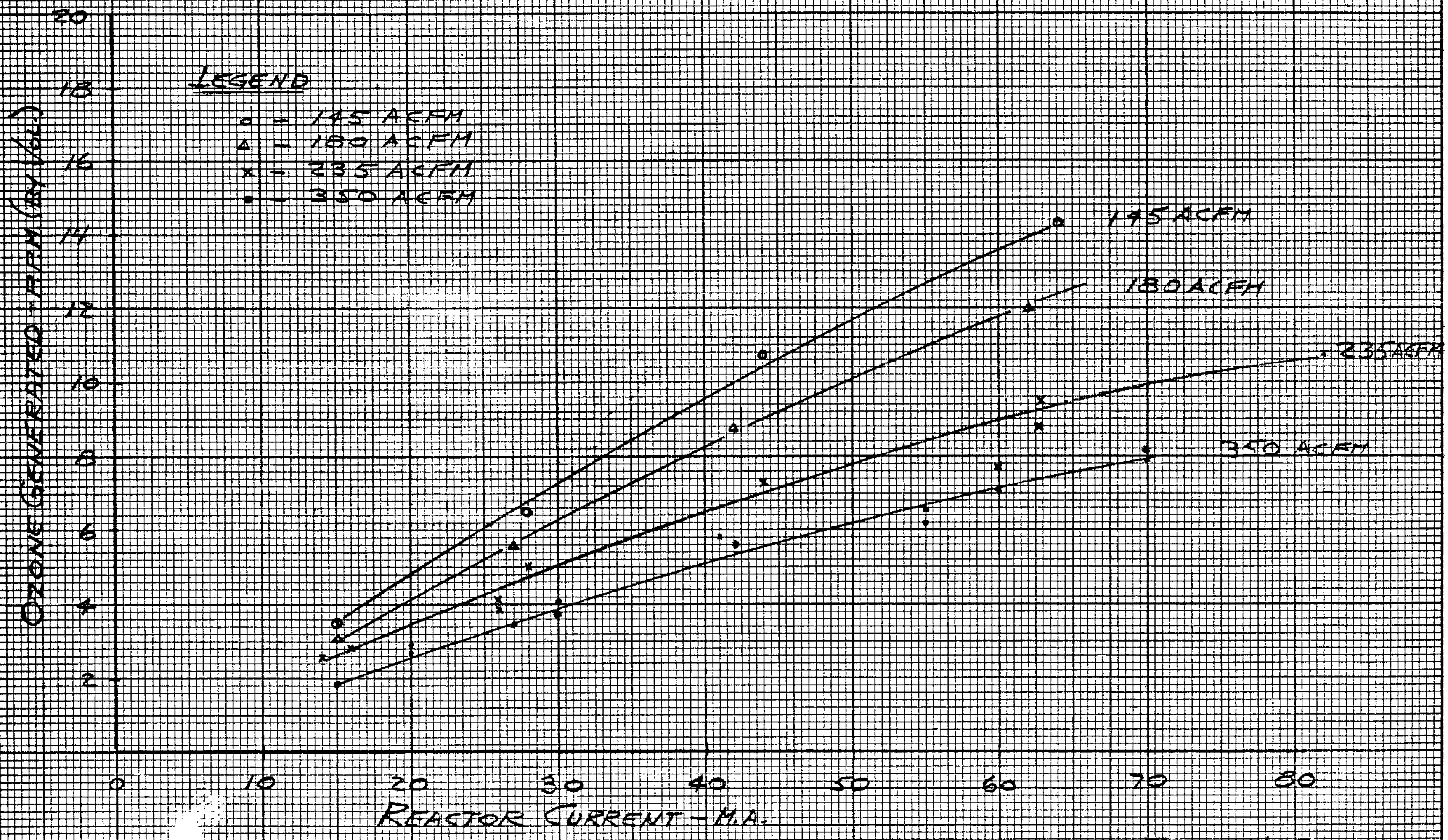


FIGURE № 8

SO2 Injection Rates

Gaseous SO_2 was injected from pressurized cylinders into the system through a calibrated rotameter and disc type mixing chamber located at the inlet duct to the reactor. SO_2 injection rates were established by SO_2 analysis of air samples drawn from the reactor inlet and outlet sampling stations.

The analysis technique utilized involved aspirating a metered gas sample through an absorption bubbler containing 250 ml. distilled water in which was dissolved 1 to 5 ml. of 1N iodine solution. Sampling was continued until the solution became colorless. The total metered air volume was then converted to standard conditions (32°F & 29.92" Hg.) and the SO_2 concentrations of the air stream calculated (P.P.M. by volume) by the following relationship.

$$SO_2 = \frac{0.000395\ (\text{ml. } 1N^{I}2)}{\text{std. cu. ft. air sampled}} = \frac{.000395\ (\text{ml.})}{\text{S.C.F.}}$$

In an initial attempt to both calibrate the rotameter and determine the efficiency of the SO_2 sampling technique, a series of fourteen (14) tests were obtained by simultaneous sampling at the reactor inlet and outlet test stations. Varied rotameter settings were investigated at a constant reactor air flow rate of 320 A.C.F.M. The results of these tests are summarized on Table No. 2 and plotted on Figure No. 9.

The accuracy of this method was high, hence on all subsequent tests for SO_3 determinations, SO_2 analysis was obtained at the inlet sampling station only.

With the equipment utilized, minimum and maximum SO_2 injection rates were in the order of 100 and 560 P.P.M. by volume respectively.

TABLE 2. SUMMARY OF SO_2 INJECTION TESTS

		Inlet Station				Outlet Station					
Date	Test No.	Sampl. Time	Quant. Sampl.	I_2 Used	SO_2 Conc.	Sampl. Time	Quant. Sampl.	I_2 Used	SO_2 Conc.	SO_2	R.M. Setting
1964		Min.	SCF	ml 1 N	ppm by vol.	Min.	SCF	ml	ppm	PSIG	
11/2	1	6	1.46	1	269	6	1.51	1	262	24	5
11/2	2	12	2.54	1	155	11	2.57	1	153	26	2
11/2	3	16	3.46	1	114	15	3.50	1	113	28	1
11/2	4	8	1.80	2	440	7	1.77	2	446	28	9
11/2	5	5	1.13	1	350	5	1.13	1	350	28	7
11/2	6	8	1.66	2	475	7.5	1.59	2	496	28	10
11/2	7	10	1.90	1	208	10	1.92	1	206	28	3.5

SO$_2$ INJECTION TESTS

ROTAMETER CALIBRATION

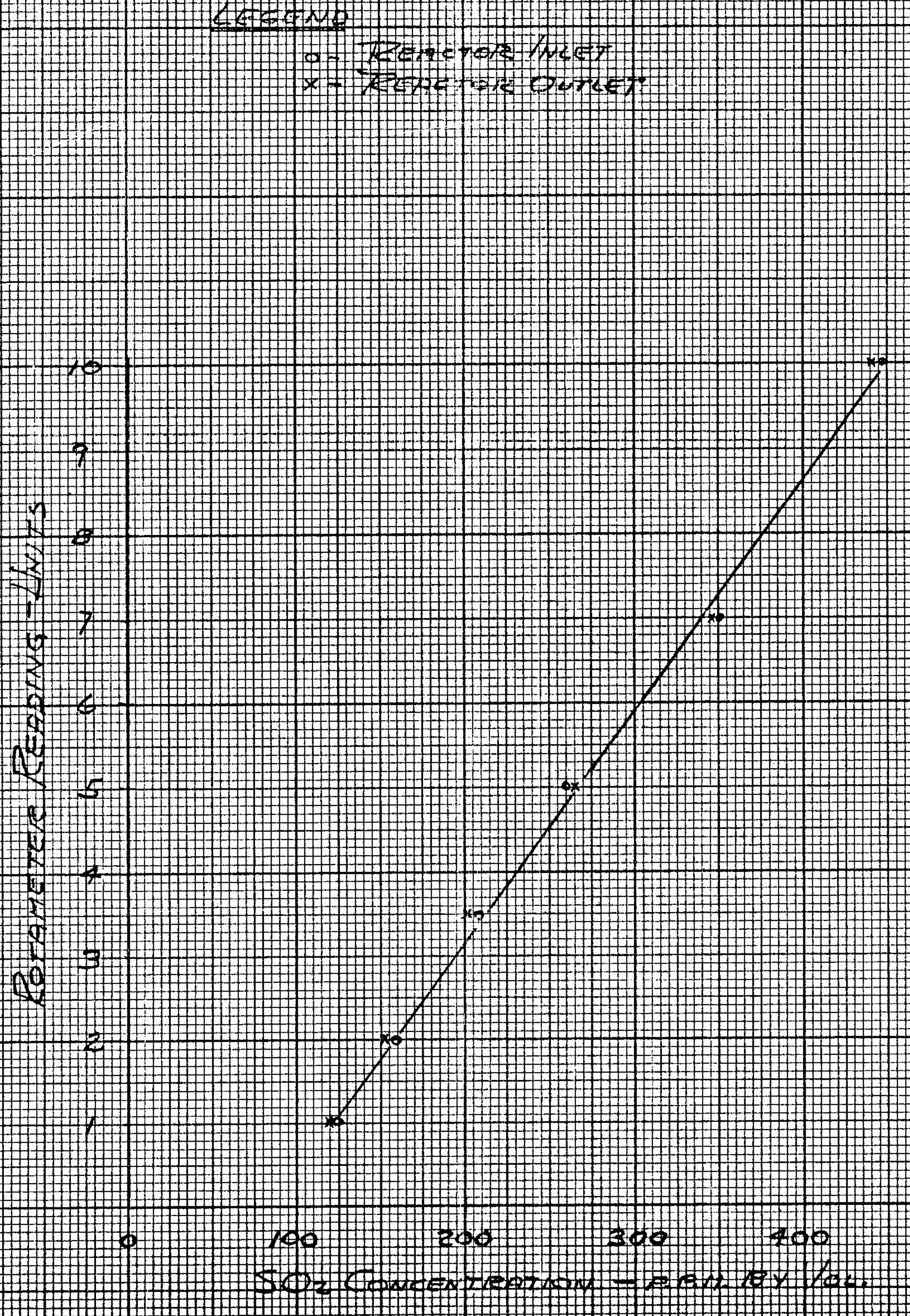


FIGURE No 9

SO_3 Determinations

The following technique was utilized for analyzing and reporting the SO_3 concentrations of the reactor exhaust air. During each test a metered gas volume was aspirated, at a rate of approximately 0.2 cfm for 20 minutes, through an absorption train comprised of two bubblers in series and followed by a glass wool filter. Each bubbler contained 100 ml. of distilled water and 100 ml. 80% isopropyl alcohol. The purpose of the alcohol was to inhibit the absorption of SO_2, and the packed glass wool filter was included to trap any entrained SO_3 mist carried over from the bubblers. At the conclusion of each test run, the total metered air volume was converted to standard conditions (32°F & 29.92" Hg.). The combined liquid sample plus the glass wool washings, diluted to a total volume of 500 ml. was then boiled to approximately a 100 ml. volume to drive off both the alcohol and any absorbed SO_2 gas. The remaining liquid was next acidified with 5 ml. of dilute hydrochloric acid (HCl) and then treated with 10 ml. of a 20% barium chloride solution ($BaCl_2$) in order to precipitate the dissolved SO_3 as barium sulphate ($BaSO_4$). After cooling to room temperature the solid precipitate was filtered from the acid solution onto a millipore paper filter and weighed.

The SO_3 concentration of the exhaust air stream was then calculated (P.P.M. by vol.) by the following relationship.

$$SO_3 = \frac{.0034 \text{ (grams } BaSO_4)}{\text{std. cu. ft. air sampled}} = \frac{.0034 \text{ (grams)}}{\text{S.C.F.}}$$

Final Overall Test Procedure

After establishing the above individual techniques for O_3, SO_2 and SO_3 measurements, a series of twenty-four (24) tests were obtained in order to evaluate the SO_2 to SO_3 conversion characteristics of the system. These tests were obtained at two gas flow rates (240 and 320 ACFM), three SO_2 concentration levels (100, 300 and 500 P.P.M.) and four electrical power inputs (200, 400, 800 and 1200 watts).

The procedure for each test run was as follows:

1. Determine air flow rate through reactor by orifice plate manometer readings and inlet and outlet air temperatures.

2. Establish electrical power inputs to the reactors by adjusting transformer tap setting and measurements of reactor voltages and currents.

3. Establish SO_2 input level by primary setting of SO_2 cylinder pressure and rotameter.

4. Sample reactor inlet air for actual SO_2 concentration level.

5. Concurrent sampling of reactor outlet gas for SO_3 concentration level, then conduct laboratory analysis of sample.

6. Ozone concentration determined from reactor electrical readings and previous calibration curves.

SUMMARY OF SO_2 - SO_3 CONVERSION TESTS

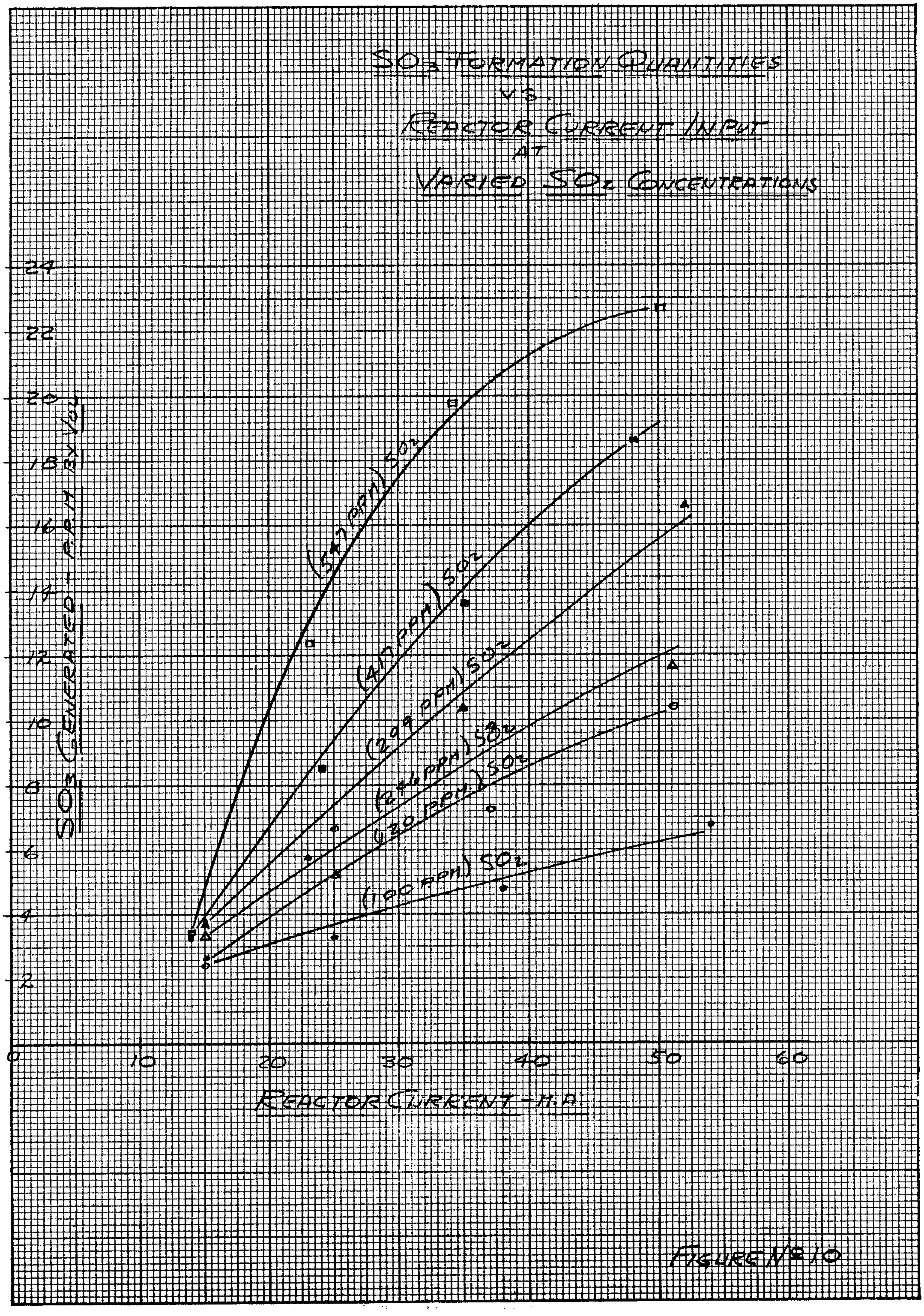
Summarized in Table 3 are the results of all the test data obtained during the twenty-four SO_2 to SO_3 conversion tests. This tabulation includes inlet SO_2 concentration levels, reactor electrical power inputs, outlet SO_3 concentrations and calculated conversion efficiencies of SO3 obtained vs. theoretical conversion of all the ozone generated in the reactor.

Plotted on Figure No. 10 is the test data relationship of the concentration of SO_3 generated vs. the electrical current input to the reactor at varied SO_2 concentration levels at the two gas flow rates investigated. The SO_3 concentrations obtained are a direct function of both the electrical power input and SO_2 concentration of the gas treated.

Figure No. 11 is a plot of the relationship of the SO_3 conversion efficiencies obtained for both gas flow rates vs. the SO_2 concentration levels of the reactor inlet air. It is evident that the conversion efficiency increases, almost linearly between SO_2 concentration levels of 100 to 400 P.P.M. by volume and thereafter is a function of the electrical power input to the reactor.

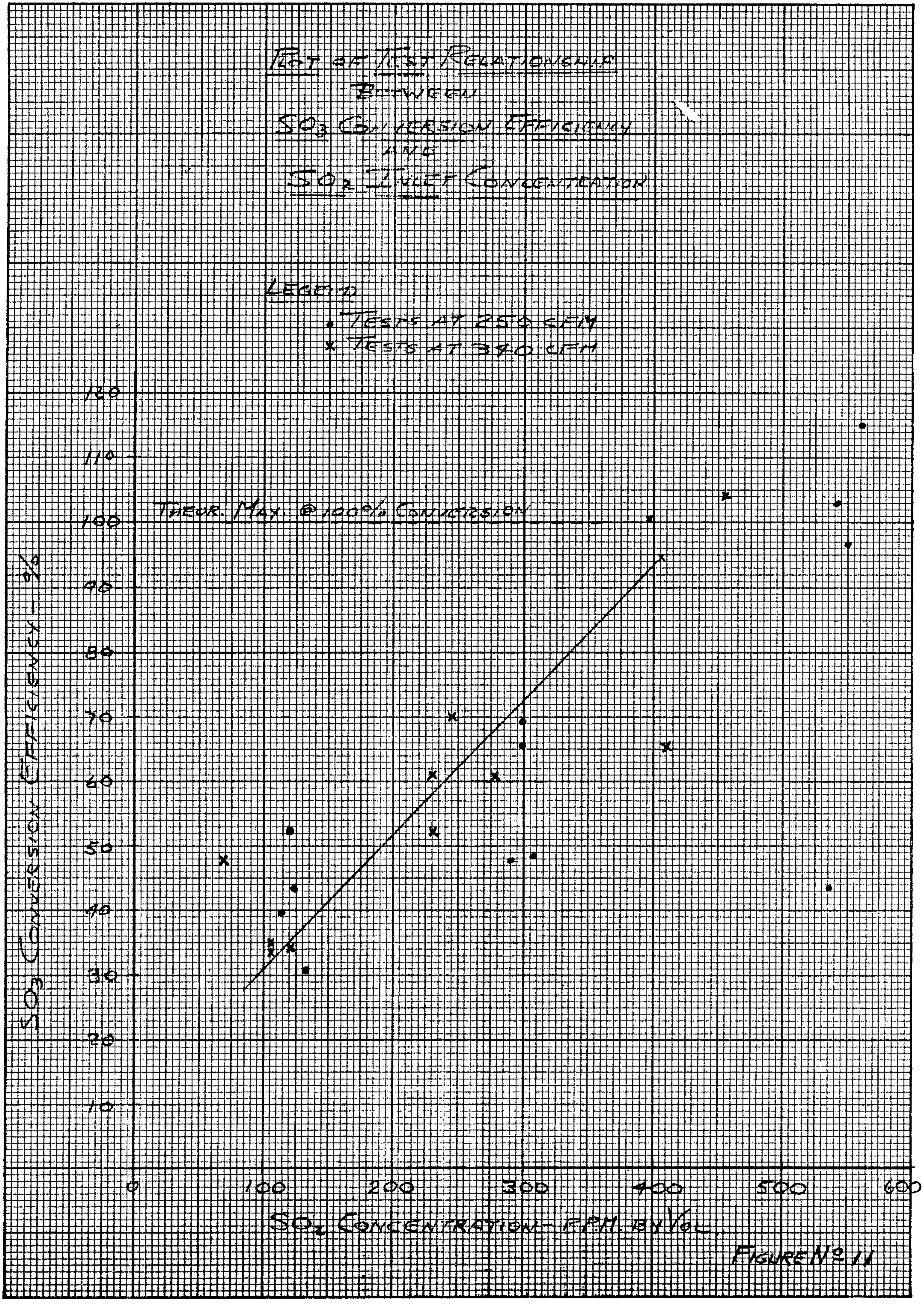
TABLE 3. SO3 CONVERSION TESTS - SUMMARY OF RESULTS

Date	Test	SO_2	Elect. Input		Actual SO_3	Orifice P	Air Temp. °F		Air Vol.	Calc. O_3	Theor. SO_3	% Conversion
1964		PPM	KV	ma	PPM	"H_2O	In	Out	ACFM	PPM	PPM	
12/26	A	131	24	15	2.40	.506	74	78	250	2.6	7.8	30.8
12/26	B	120	28	25	6.65	.506	75	83	250	4.2	12.6	52.8
12/26	C	113	33	37	7.25	.506	75	90	250	6.1	18.3	39.6
12/26	D	122	37	51	10.40	.506	75	99	250	8.0	24.0	43.2
11/28	E	74	23	15	2.60	.875	75	78	345	1.8	5.4	48.2
11/28	F	119	28	25	3.28	.875	75	82	345	3.2	9.6	34.3
11/28	G	103	32	38	4.83	.885	75	87	345	4.8	14.4	33.5
11/28	H	104	38	54	6.90	.890	75	93	345	6.6	19.8	34.8
12/26	I	290	24	15	3.7	.506	74	78	250	2.6	7.8	47.5
12/26	J	309	28	23	5.8	.506	74	82	250	4.0	12.0	48.5
12/26	K	295	32	35	11.4	.506	74	88	250	5.8	17.4	65.2
12/26	L	300	37	52	16.6	.510	76	100	250	8.0	24.0	69.2
11/27	M	230	24	15	3.3	.870	76	79	345	1.8	5.4	61.0
11/27	N	229	28	25	5.2	.875	76	83	345	3.2	9.6	52.5
11/27	O	246	33	37	9.9	.880	76	87	345	4.7	14.1	70.0
11/27	P	278	37	52	11.7	.885	76	92	345	6.4	19.2	60.5
12/26	Q	537	24	14	3.4	.506	75	78	250	2.6	7.8	43.5
12/26	R	540	28	23	12.3	.510	74	82	250	4.0	12.0	103.0
12/26	S	560	32	34	19.8	.510	75	88	250	5.7	17.1	115.0
12/26	T	550	37	50	22.6	.510	75	98	250	7.8	23.5	96.5
11/26	U	412	23	14	3.5	.855	75	79	340	1.8	5.4	65.0
11/26	V	403	28	24	8.5	.855	75	82	340	3.0	9.0	94.5
11/26	W	392	33	35	13.6	.860	75	87	340	4.5	13.5	101.0
11/26	X	460	36	48	18.6	.870	75	92	340	6.0	18.0	104.0



SO$_3$ FORMATION QUANTITIES
VS.
REACTOR CURRENT INPUT
AT
VARIED SO$_2$ CONCENTRATIONS

FIGURE Nº 10



PLOT OF TEST RELATIONSHIP
BETWEEN
SO₃ CONVERSION EFFICIENCY
AND
SO₂ INLET CONCENTRATION

FIGURE Nº 11

SUMMARY OF RESULTS

It was assumed at the outset of the investigation that below the dew point of SO_3 (115°F) SO_2 gas in the presence of ozone, created by an electrical corona discharge, would predictably react in stoichiometric quantities to form SO_3 by the following chemical reaction:

$$3SO_2 + O_3 = 3SO_3$$

It was anticipated that for every volume of ozone generated, three volumes of SO_3 would be produced if three theoretical volumes of SO_2 were present for reaction.

The results of the subject investigation indicate that ozone is generated in quantitative amounts which are directly proportional to the "corona" current and inversely proportional to the air flow rate through the reactor. For the electrical reactor used in this investigation, the rate of ozone generation is expressed by the following empirical relationship:

$$O_3 = \frac{37I}{V}$$

SO_3 yields, however, are dependent upon both the concentrations of ozone and the concentrations of SO_2 present in the treated air passing through the reactor. The theoretical SO_3 yields appear to vary from 30 to 100% almost linearly with SO_2 concentrations for any given ozone concentration level between the ranges of 100 to 400 P.P.M. SO_2. Above 400 P.P.M. SO_2, the SO_3 yield is 100% of theoretical, is independent of SO_2 concentrations, and is a direct function of the above concentrations.

The following empirical relationships are indicated for the rate of SO_3 generation in the system investigated:

SO_2 Concentration Levels (100 - 400 P.P.M.)

$$SO_3 = 3(37)\ \frac{I}{V}\ \frac{SO_2}{400} \quad \text{or} \quad SO_3 = 0.278\ \frac{(I)\,(SO_2)}{V}$$

SO_2 Concentration Levels (above 400 P.P.M.)

$$SO_3 = \frac{101\,I}{V}$$

where = SO_3 = P.P.M. by Vol.
SO_2 = P.P.M. by Vol.
I = Reactor Current - ma
V = Air Flow Rate - A.C.F.M.
O_3 = P.P.M. by Vol.

DISCUSSION OF RESULTS

Ozone Generation

The pilot plant precipitator was operated at air flow rates varying from 145 to 350 ACFM comparable to mass flow rates of 10.9 to 26.2#/min. Reaction time in the precipitator varied from 0.305 to 0.126 sec. Electrical energy input was varied at each flow rate from 335 to 2400 watts. Ozone production values ranged from a minimum of 0.004 to a maximum of 0.02#/hr. This is an energy consumption of 71.5 to 140 KW-HR per pound of ozone generated equivalent to 6550 to 1280 K cal./mol. ozone.

In commercial ozonators the yields obtained in air are reported as approximately 8.3 KW-HR per # 0_3 equivalent to 760 K cal. per mol. The pilot precipitator investigated therefore produces equivalent ozone quantities at energy consumption levels 8.8 to 16.8 times that of a commercial ozonator and 56 to 180 times theoretical minimum threshold requirements. Optimum ozone generation rate was 0.02#/hr. at an energy consumption level of 113 KW-HR per # 0_3 when the precipitator was operated just below the "spark-over" point with a treatment time of 0.126 sec.

In a commercial precipitator, however, this ozone generating capability is a by-product of the basic process in that the electrical fields are primarily designed to ionize suspended mist or dust particles in air or gas streams and electrostatically deposit these charged particles upon grounded surfaces. A secondary capability therefore exists for reaction of this by-product ozone with objectionable gaseous components present in the gas stream passing through the precipitator.

SO_2 Conversion

The SO_2 formation tests obtained in the pilot precipitator indicated that the mechanism of the reaction of ozone with SO_2 is rather complex with O_3 conversion efficiencies varying from 30% up to 100%. The efficiency appears to be primarily dependent upon the SO_2 concentration levels rather than the mol. ratios of SO_2 to O_3.

At low SO_2 concentration levels (100 PPM) and SO_2/O_3 mol. ratios of 15 to 50, the following reaction appears to be favored.

$$SO_2 + 5O_3 = 7O_2 + SO_3$$

At high SO_2 concentration levels (400 PPM) and SO_2/O_3 mol. ratios of 70 to 150 the following reaction is predominant.

$$3SO_2 + O_3 = 3SO_3$$

At SO_2 concentration levels between 100 and 400 PPM and SO_2 to O_3 mol. ratios of 35 to 120 combinations of both of the above reactions occur. The efficiency with which O_3 is reacted with SO_2 in these concentration ranges is directly proportional to the SO_2 concentration level.

COMMERCIAL EVALUATION

Utilizing known electrical design characteristics of commercial precipitators the ozone generating characteristics of a hypothetical installation were estimated from the results of the above pilot precipitator work. These hypothetical conditions were established as follows:

Design removal of entrained dust particles - 99.5%.

Gas to be treated in installation - 226,000 ACFM air.

Gas velocity in installation - 6 ft./sec.

Gas retention time in installation - 4.5 sec.

Total energy input to precipitator as a dust collector - 72 KW.

Assumed ozone generating characteristics = 113 KWH/#O_3.

On the above basis then, the commercial Cottrell dust collector could be expected to produce a maximum of 0.65# ozone per hour. This would be available to react with gaseous constituents such as SO_2 and convert it to SO_3 which could, in the presence of atmospheric moisture, combine to H_2SO_4 mist and be recovered in the collector along with the suspended dust particles.

Assuming that the most favorable SO_2-O_3 gaseous reaction occurs, namely $3SO_2 + O_3 = 3SO_3$, on a weight basis then each pound of ozone formed could react with 4# SO_2 to form 5# SO_3

which in the presence of water vapor could form 6.12# H_2SO_4 mist. For the hypothetical example utilized above the precipitator is expected to generate 0.65#/hr. of ozone and convert 2.6#/hr. of gaseous SO_2 to 3.98# H_2SO_4 mist which would be removed from the air stream while treating a total air flow rate of 1,098,000#/hr. With this possibility, gaseous SO_2 concentrations in the order of 24 PPM (by weight) (1/06 PPM by volume) could be completely removed from the gas stream as a by-product of the normal dust removal portion of the process.

It was, however, previously determined that complete reaction of O_3 with SO_2 occurred to form SO_3 at levels above 400 PPM SO_2 by volume. Below this value yields decreased to 30% at 100 PPM SO_2 by volume concentrations. These results indicate that complete reaction of O_3 could only occur at high SO_2 concentration levels (+400 PPM SO_2) and at these levels SO_2 concentration reduction is under 1%. On a commercial basis then the process is evidently impractical in that high levels of SO_2 concentrations are necessary for efficient conversion of ozone. Under these favorable conditions, although 100% of the O_3 is utilized, under 1% of the SO_2 is converted to SO_3.

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