# ABSTRACT

Title of Thesis : The Dry Removal Process of Sulfur Dioxide
From Flue Gases Using Aluminum Oxide

Ching-Hwang Lu , Masterof Science in Chemical Engineering, 1984

Thesis directed by : Dr. W. T. Wong, Assistant Professor,
Chemical Engineering

Oxidation of sulfur dioxide to sulfur trioxide and absorption on aluminum oxide pellet as a mean of removing sulfur dioxide from flue gas was studied in a packed bed reactor at various temperatures, residence times, $SO_2$ inlet concentrations ( ppm level ), and particle sizes. Three different experiments were conducted : (i) sulfation with oxygen/ozone, (ii) sulfation with oxygen only in the presence of UV radiation ( 254 nm or 366 nm ), (iii) sulfation with oxygen only. In all the experiments substantial absorption of sulfur dioxide by alumina pellet was observed. Sulfation with oxygen/ozone give the highest absorption of $SO_2$, followed by sulfation with oxygen in the presence of UV radiation, while sulfation with oxygen only had the lowest absorption. In all these experiments, the absorption of $SO_2$ decreases with increasing $SO_2$ concentration , increases with increasing residence time, and increases with decreasing particle size. At $SO_2$ concentration of 8,352 ppm, residence time of 0.018 sec., and particle size of 0.3175 cm, sulfation with oxygen/ozone and sulfation with oxygen only in the presence of UV radiation attain maximum absorption at about 275°C, whereas sulfation with oxygen only attains maximum absorption at about 640°C.

# The Dry Removal Process Of Sulfur Dioxide From Flue Gases Using Aluminum Oxide

by

Ching-Hwang Lu

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirement for the degree of Master in Science in Chemical Engineering

1984

# APPROVAL

Title of Thesis : The Dry Removal Process of Sulfur Dioxide From Flue Gases Using Aluminum Oxide

Name of Candidate : Ching-Hwang Lu
Master of Science in Chemical Engineering,
1984

Thesis and Abstract Approved : ______________________ ________
Dr. W. T. Wong    Date
Assistant Professor
Chemical Engineering

Signature of other members
of the thesis committee

# VITA

Name : Ching-Hwang Lu

Permanent address :

Degree and date to be conferred : Master of Science, 1984

Date of birth :

Place of birth :

Secondary education :

| Collegiate institution attended | Dates | Degree | Date of Degree |
|---|---|---|---|
| New Jersey Inst. of Tech. | Sept., 1982 | M. S. | Oct., 1984 |
| National Taipei Inst. of Tech. | Sept., 1974 | B. S. | June, 1979 |

Major : Chemical Engineering

Position held : Rearch Assistant in the Department of Chemical Engineering, N.J.I.T., Newark, N.J., U.S.A.

# ACKNOWLEDGMENT

The author is most greatful to his advisor, Dr. w. T. Wong who has contributed in so many ways to make this research a great success.

My special thanks go to Dr. D. Tassios, for his thoughtful advices, helpful suggestions and ideas in conducting this research.

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

Table Page

# NOMENCLATURE

$a$ = Weight of solid, at time 0, gram

$b$ = Weight of solid, at time t, gram

$F_{SO_2}$ = Molar flow rate of $SO_2$, mole/min.

$K$ = Equilibrium constant

$M_1$ = Molecular weight of $AL_2O_3$

$M_2$ = Molecular weight of $AL_2(SO_4)_3$

$Q_{O_2/O_3}$ = Flow rate of $O_2/O_3$ at 70°C, 8 psig, $ft^3$/min.

$t_c$ = Contact time of $SO_2$ with solid, min.

$V_{SO_2}$ = The reading of the mass flow meter, volt

$W_s$ = Weight of sample, gram

$X_{10}$ = Number of moles of $AL_2O_3$ at time 0

$X_1$ = Number of moles of $AL_2O_3$ at time t

$X_2$ = Number of moles of $AL_2(SO_4)_3$ at time t

$\tau$ = Residence time, sec.

$\varepsilon$ = Fractional void of the Packed bed.

cfm = Cubic feet per minute

sccm = Cubic centimeter per minute at STP

# INTRODUCTION

Within the past decade a realization has evolved concerning the removal of sulfur dioxide from industrial processes so as to cut down on harmful pollutants entering our atmosphere. Perhaps the largest source of $SO_2$ emissions in this country besides oil refineries can be attributed to the electrical power plants, where approximately 55-56% of the electrical energy produced utilizes coal or petroleum (1). In accordance with the Clean Air Act (1972), removal of sulfur oxides from stack gases or the removal of sulfur from coal or sour crude oil is mandated (2).

In the past few years a variety of processes(3,4) have been proposed to eliminate this problem. These processes can be summarized as follows:

(1) Wet Scrubbing Systems
    a. Throwaway- Lime, Limestone, Double Alkali (Sodium Sulfite and Sodium Sulfate).
    b. Regenerable-$KHSO_3$ Scrubbing (Wellman-Lord), Oxidation Scrubbing (Catox), Stauffer's Phosphate, MgO Scrubbing (Magox).
(2) Dry Sorption Systems
    a. Throwaway- Fluidized bed combustion in limestone beds.
    b. Regenerable- Activated carbon, Alkalized alumina.

Most of these processes involve the introduction of some material into the gas stream to combine with the sulfur oxides and convert them to a removable liquid or solid. However,due to some drawbacks of wet scrubbing systems, such as the disposal of the liquid or solid waste, equipment corrosion, and additional energy costs for blowers and post-heaters of wet scrubbing systems in which an alkali solution is used to remove the sulfur oxides, a dry method of removal has been the main objective of industry.

To remove $SO_2$ in a dry process many studies (5,6,7) have been done on various solid sorbents such as metal oxides. However, the reaction kinetics for $SO_2$ sorption are extremely slow, due to the difficulty of permeation of $SO_2$ into the solid particle interior. If regeneration is involved, the particles tend to become inactivated and deteriorate physically over several cycles of sorption and regeneration. Thus, without the delibrate oxidation of $SO_2$ to $SO_3$, the removal of $SO_2$ by a gas-solid sorption process appears elusive. A sorbent was sought which would eliminate these problems. In 1971, upon more considerations of various metal oxides capable of regeneration, aluminum oxides was seleted at N.J.I.T..

THis process for $SO_2$ removal involves: firstly conversion of $SO_2$ to $SO_3$ and then absorption on aluminum oxide to form aluminum sulfate, and regeneration of the resulting aluminum sulfate with CO to yield alumina and sulfur. This process is a " dry " one since no water solution or slurries are involved and it has the following advantages over the " wet " processes:

(1) Minimum corrosion problems and reheating of flue gas before they are discharged to the atomosphere.
(2) No fluid is employed anywhere.
(3) No solid waste problem since the only solid product sulfur, can be marketable.
(4). Estimated lower coats.
(5) There is a large and cheap supply of alumina. Moreover, the used alumina can be regenerated if necessary.

The adsorption reaction of the process have been examined fairly entensively. Toscano(8) showed that the a particle size of 0.017 in. could be reacted to completion in 4 hours and a particle size of 0.025 in. could be reacted to 90 % of copmletion in the same time. Stewart (1) performed an economic evaluation of this process and showed that the dry process have lower cost of electricity than the wet scrubbing processes. Yildirim(9) conducted extensive sulfation by using $SO_3$ vapor, carried by $N_2$ and reacting with aluminum oxide placed in a basket type reactor. He determined that the overall reaction kinetics and mass transfer follow the single pore model of Ramachadon (10). It was discovered that the reaction is first order with respect to $SO_3$. Yildirim also found that sulfation proceeds to 100% completion for an alumina particle size of 0.0294 cm or less. However, there are some problems unsolved. Those are:

(1) $SO_3$ tends to polymerize into a highly viscous brown liquid which will be absorbed by alumina particles, if water vapor exists in the system.

(2) $SO_3$ will decompose to $SO_2$ and $O_2$ at high temperature (11). $N_2$, $SO_2$, $O_2$, and $SO_3$ may be absorbed, physically or chemically, by alumina oxide.

(3) In high flow rate, the basket suspended in the top of the reactor vibrates in the turbulent inlet gas stream and thereby renders the data unreliable.

Because of the above shortcomings, some experimental improvements have been done in this work:

(1) Direct reaction of $SO_2$ and $O_2$ on alumina was studied instead of using $SO_3$ vapor.

(2) A packed-bed tubular reactor was used instead of the basket-type reactor, thus greatly improving weighing accuracy.

(3) $O_2$ was used as inert gas to dry the system before starting the reaction.

(4) Physical adsorption factor can be eliminated by

purging the reactor with $O_2$ before weighing.

The main objective of this work is to study the removal of $SO_2$ from flue gas by absorption on alumina. Since a proper understanding of the behavior of the reaction is necessary for design purposes, the effect of different particle sizes of alumina, temperature, residence time, and $SO_2$ concentration on the adsorption of $SO_2$ and conversion of alumina to aluminum sulfate were studied. Besides, it was sought to experimentally demonstrate that high degree of adsorption or conversion could be achieved for industrial purposes.

In the study of noncatalyzed gas-phase reaction between $SO_2$ and $O_2$ by Cullis, Henson, et al.(12), the collisional activation energy of $SO_2$ molecules is found to be 75 Kcal/gmole. However, according to the Maxwell-Boltzman distribution law at ordinary temperature, only about one in $10^7$ molecules of a gas possesses a kinetic energy equivalent to 25 Kcal per mole. Therefore, reaction whose activation energy is larger than this value will be slow. The absorption of UV light may readily supply the molecules with far greater amounts of energy so that the photochemical reaction may be rapid. This is demonstrated by the study of Paul, Lutsep, et al.(13). The potochemical reaction of sulfur dioxide in air in the presence of water vapor up to 100% relative humidity is of the order of 0.1% per hour in the presence of UV irradiation equivalent to noonday sunlight intensities. On the contrary, there is no reaction when the gaseous mixture of sulfur dioxide and air is kept in the dark for day. Two different wave lengths, 254nm & 366nm, were used in this study to investigate the possibility of accelerating the absorption rate of $SO_2$ by alumina in the presence of oxygen and /or ozone. The possibility that ozone might react with sulfur dioxide to form sulfur trioxide rapidly and in appreciable quantity has been recognized since the start of this century A recent report by Slatter & Rizzone (14) showed that the oxidation of $SO_2$ by $O_3$ in a dry flue gas is rapid. At $370^oC$ a 50% conversion was achieved in a CSTR, whereas, from a study by Culli, Henson et al. (12), the formation rate of $SO_3$ in noncatalyzed gas phase reaction between $SO_2$ and $O_2$ was found to be approximately $7.2 \ X \ 10^{-6}$ mole $liter^{-1} \ min^{-1}$. Thus, we have concluded that the use of ozone should increase the formation rate of $SO_3$ and thereby increase the absorption rate of $SO_2$ by alumina.

# EXPERIMENTAL

## A. APPARATUS

The description of the complete sulfation apparatus is divided into the following areas:

- OVERALL PROCESS LAYOUT & BASIC OPERATION
- OZONE GENERATOR
- FLOW & FLOW CONTROL OF $SO_2$ & $O_2/O_3$ FLOW STREAMS
- REACTOR DESIGN

### OVERALL PROCESS LAYOUT & BASIC OPERATION

A schematic diagram of the overall sulfation process is given in FIGURE 1. The desired operation of the sulfation apparatus is to have $SO_2$ & $O_2/O_3$ mixture passing at a known flow rate, through the reactor which is maintained at a known uniform temperature. The mixture will react with the $AL_2O_3$ packed in the reactor. After a period of reaction, the reaction is stopped by purging with $O_2$, and the entire reactor, in the form of a 6 mm O. D. quartz tube, is weighed by hanging under a Sartorius balance. Any unreacted gas is stripped of $SO_3$ vapor by passing through an ice trap before vented into the hood.

### OZONE GENERATOR

The $O_2$ was fed to a Welsbach ozone generator (15), in which up to 4% of the $O_2$ was converted to $O_3$. The Welsbach

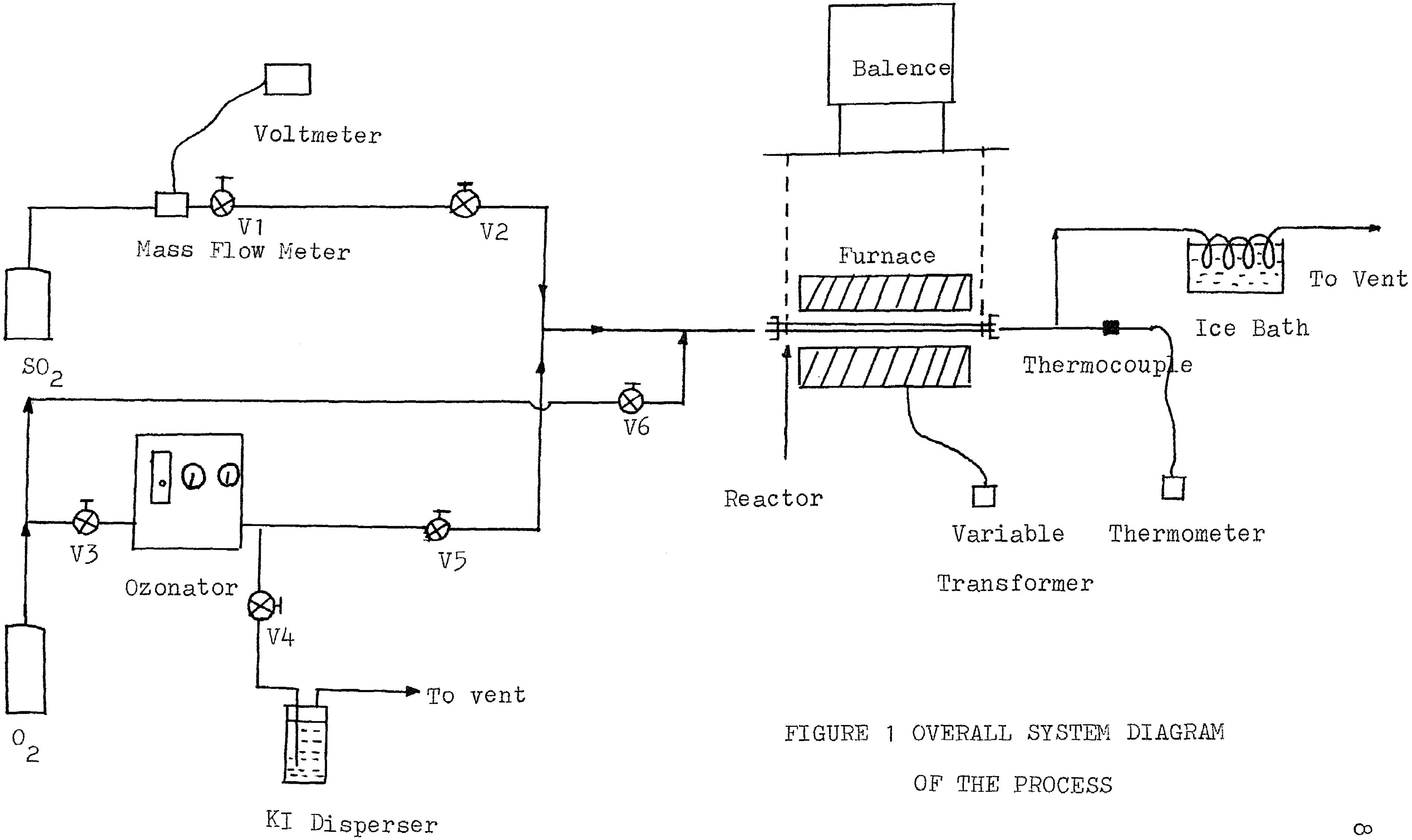


FIGURE 1 OVERALL SYSTEM DIAGRAM OF THE PROCESS

Model I-23 Laboratory Ozontor is designed for operation on a 115 volt, 60 Hertz circuit. A transformer within the cabinet increases the voltage to the relatively high voltage necessary for ozone generation. To compensate for difference in line voltage and to vary ozonator output, a variable voltage transformer has been incorporated in the primary circuit. The input voltage to the high voltage transformer can be read on the panel voltmeter. When using the ozonator the voltage as read on this voltmeter should not be set above 115 volts. When the ozonator is in operation a water flow of about 5 gallon per hour should be maintained through the cooling jacket and oxygen pressure should be reduced to 8-10 psig by means of a suitable valve, $V_3$, ahead of the ozonator ( see FIGURE 2 & 3 ).

## FLOW AND FLOW CONTROL OF $O_2/O_3$ & $SO_2$ FLOW STREAMS

Two streams of $O_2$ from cylinder were used in this work; one was used for drying the system before the reaction and stopping reaction before weighing the reactor, the other was fed to ozone generator. Since it is necessary to know the exact $SO_2$ & $O_2/O_3$ flow rate so that the concentration of $SO_2$ can be determined, a mass flow meter and rotameter were used to measure the flow rates of $SO_2$ and $O_2/O_3$ streams respectively. The rotameter on the panel of ozonator, covering a range from 0.015 CFM to 0.16 CFM at 8 psig and 70 $^oF$, gives the flow rate of $O_2/O_3$ stream entering the reactor.

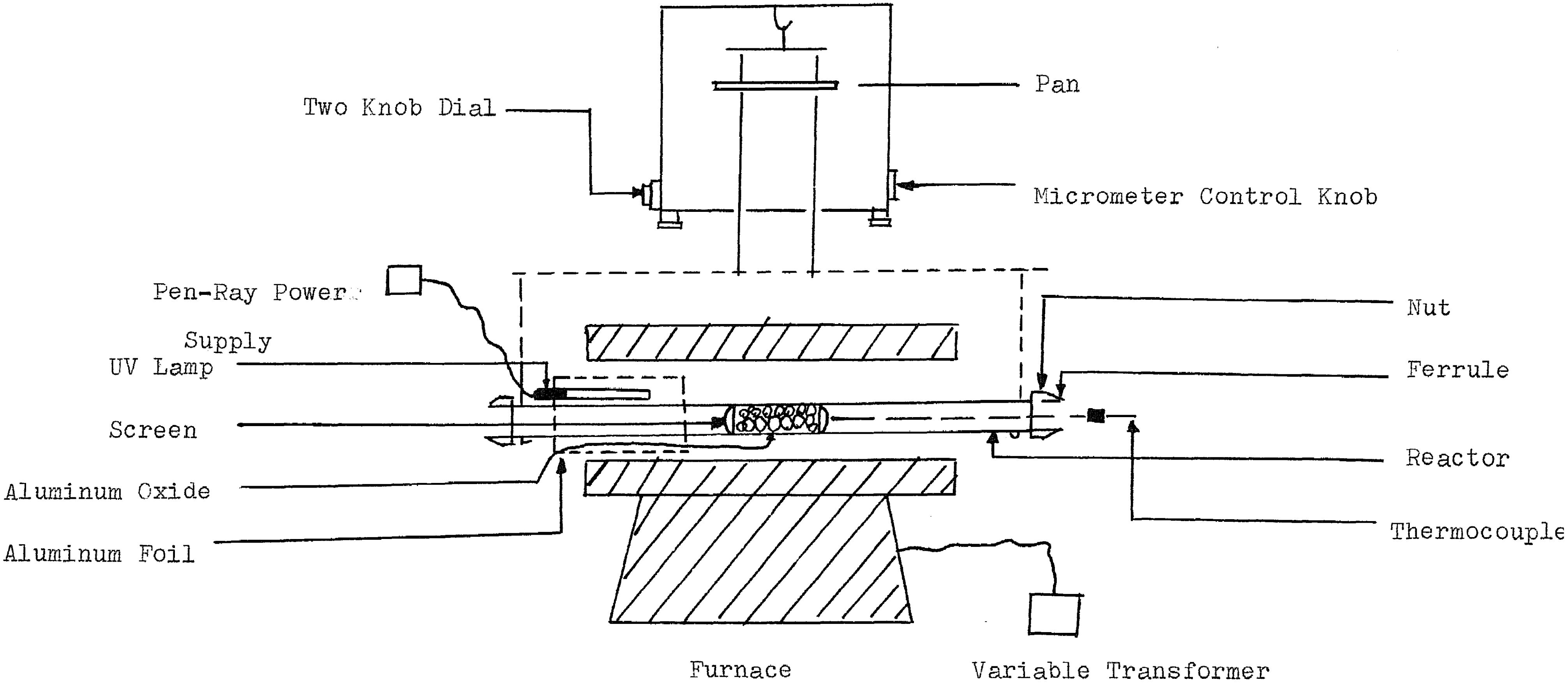
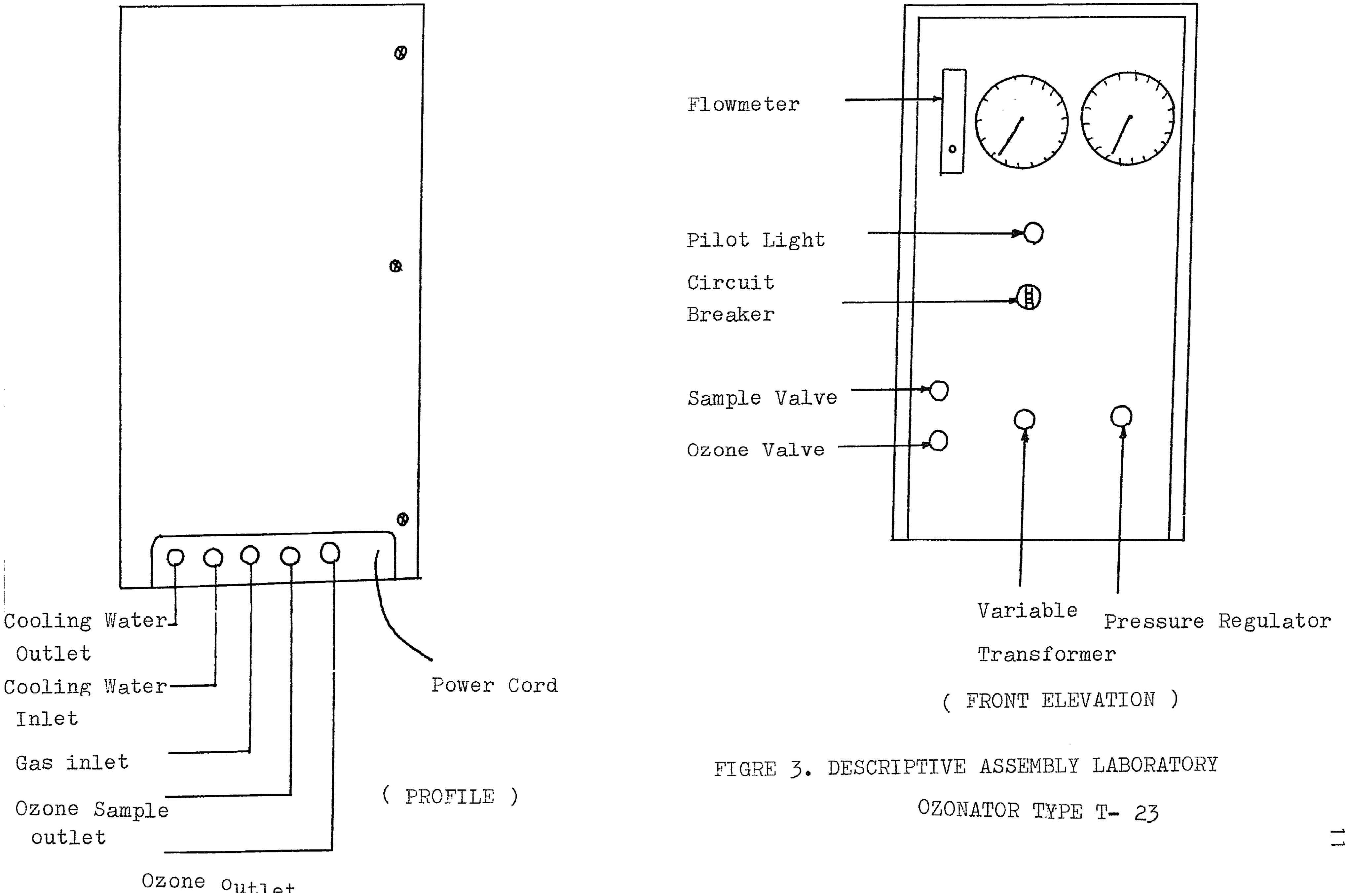


FIGURE 2. DETAILED DRAWING OF THE REACTOR WITH UV LAMP



( PROFILE )

( FRONT ELEVATION )

FIGRE 3. DESCRIPTIVE ASSEMBLY LABORATORY OZONATOR TYPE T- 23

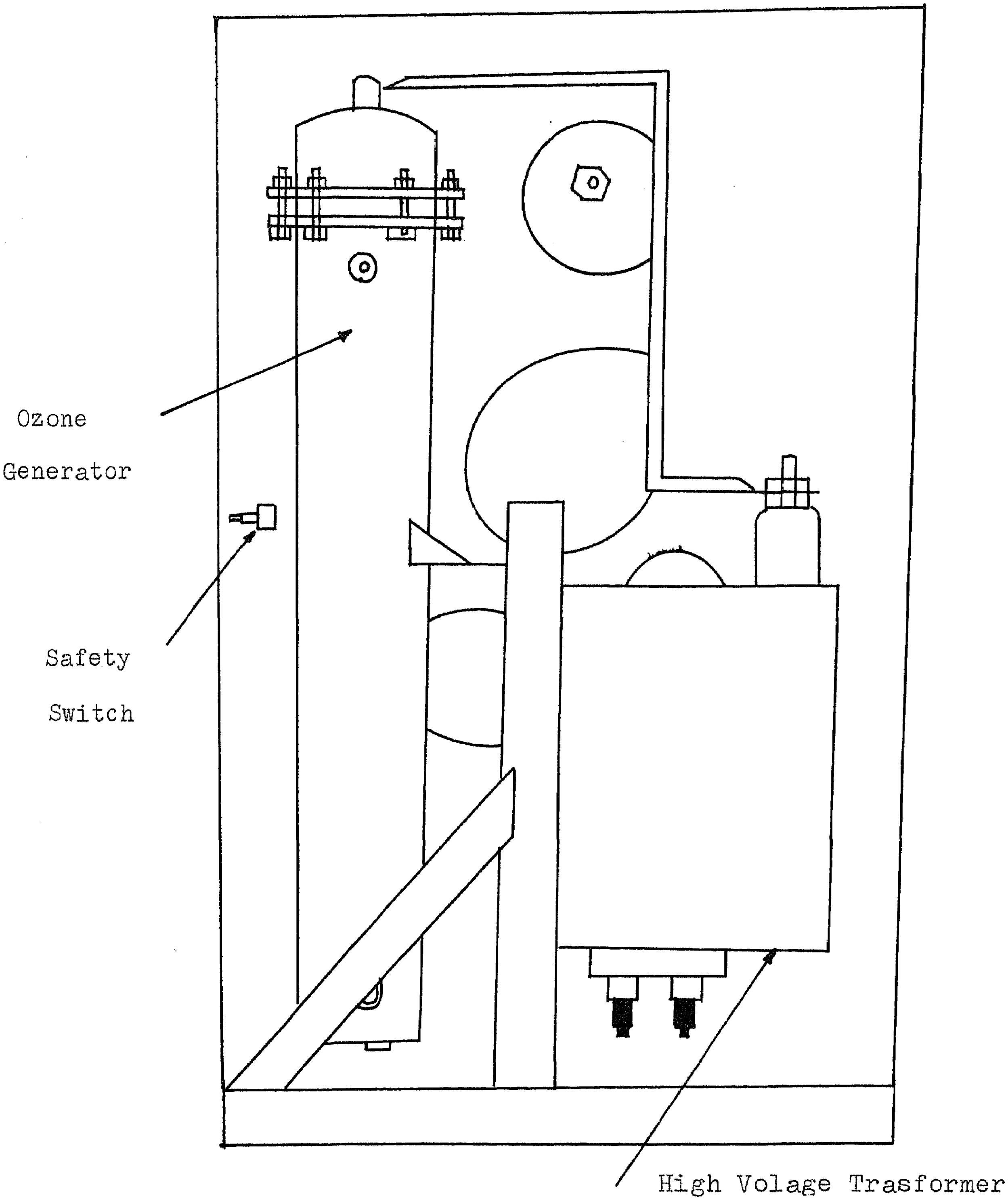


FIGURE 4. WELBACH OZONATOR REAR ELEVATION ( COVER REMOVED )

Valve V5 was used to control this stream flow. A mass flow meter,manufactured by MKS Instruments Inc, with a range of 100 sccm, was used to measure the flow rate of $SO_2$ entering the reactor . Fine adjustment of $SO_2$ flow rate was effected by the needle valve V1. The sulfation run can be initiated by turning on the $SO_2$ flow to the system. via the ON-OFF valve V2.

## REACTOR DESIGN

The reactor tube was a 16 inch long, 6 mm O.D. quartz (or pyrex) tube, having a 316 stainless steel 1/4 inch nuts and graphite ferrules on each end ( FIGURE 2 ). Quartz was chosen as the reactor material since it is inert and is able to withstand relatively high temperature up to 1200°C, for a long period of time. Alumina particles were packed in the reaction tube and held by 316 stainless steel screens to prevent entrainment by the gas stream. A Chromel-Alumel thercouple, 1/8 inches in diameter and 12 inches long , was placed inside the reactor to monitor the temperature of the sample. The thermocouple was connected to a OMEGA Model 660 digital temperature readout meter. If the temperature of the sample vary drastically , the pore structure of the particles may be broken. Therefore, it is necessary to read the weight of reactor, at a constant temperature. The reactor was suspended while still in the furnace , by a metal wire on each end of the tube which was not within the furnace. The metal wires were attached to the weighing pan of a Satorious Scale Type 2400 by passing through two 2 cm holes at the bottom of the scale.The balance was supported on a platfprm located directly above the furnace. The furnace is 13 inches long and 2 inches in diameter and is electrically operated by connected to a variable transformer. It's maximum operating temperature is 1200°C. When experimental run with UV irradiation was conducted, a Pen-Ray Lamp, manufactured by Ultra-Violet Products Inc., and connected to SCT-1 power supply, was inserted in the furnace parallel to the reaction tube. The Pen-Ray Lamp and the reactor were wrapped by aluminum foil so that the UV light could efficiently irradiate on the inlet gas stream. Two different wavelengths were used: 254 nm with an intensity of 4400 $\mu w/cm^2$ at a distance of 0.075 in. and 366 nm with an intensity of 145 $\mu w/cm^2$ at a distance of 0.075 in.

## B. ALUMINA SAMPLE AND QUALITATIVE ANALYSIS OF PRODUCT

### Alumina Samples

Alumina samples used in this work were ALCOA H-151. The samples are porous forms of aluminum oxide with high surface area. They are nontoxic and will not soften, swell or disintegrate when immersed in water. Chemical and physical properties of ALCOA H-151 are list in TABLE 1. They will absorb water from a gas of hogh humidity. Due to the high sorptive capacity of alumina at humid condition, $O_2$ and $SO_2$ used in this experiment were extra dry. The samples were prepared by drying in a furnace at a temperature of about $350^oC$ over night. Once placed in the reactor , a controlled amount of oxygen was passed through the sample and the reactor was weighed repeatedly until there is no change in weight. Samples of smaller sizes were obtained by crushing the 1/8 inch balls and the various sizes were selected by sieving over standard mesh screens.

### Qualitative Analysis of Product

From thermodynamics, the following reaction of alumina is possible (13)

$$AL_2O_3 + 3SO_2 + 1.5O_2 \longrightarrow AL_2(SO_4)_3 \qquad (1)$$

This can be demonstrated by the equilibrium constant calculations. The free energy of the reaction ($\Delta F^o$) at $298^oK$ is -147.62 Kcal/mole. According to the following equation

| ALCOA ACTIVATED ALUMINA | |
|---|---|
| Grade of activated alumina | H-151 |
| Sieve analysis, % | |
| On 3 mesh | 28. |
| 3-4 mesh | 71. |
| Through 4 mesh | 1.0 |
| Chemical analysis, % | |
| $AL_2O_3$ | 90. |
| $Na_2O$ | 1.4 |
| $Fe_2O_3$ | 0.1 |
| $Si\ O_2$ | 1.7 |
| Loss on ignition ($1100^{o}C$) | 6.0 |
| Pysical properties | |
| Surface area, sg. meter/g | 390. |
| Bulk density, loose, lb/ft$^3$ | 51. |
| Bulk density, packed, lb/ft$^3$ | 53. |
| Specific gravity, ml/g | 3.1-3.3 |
| Pore volume, ml/g | 0.3 |
| Pore diameter, A$^{o}$ | 50. |

TABLE 1. DATA FOR ACTIVATED ALUMINA SAMPLES

( DATA EXCERPTED FROM ALUMINUM COMPANY OF AMERICAN,
1501 ALCOA BUILDING, PITTSBURGH, PA. 15219 )

$$\Delta F^{o} = -RT\ln K \qquad (2)$$

then, $K_{298} = 37 \times 10^{106}$. The value of K at various temperatures is shown in the following

| T ($^{o}$K) | K |
|---|---|
| 298 | $37 \times 10^{106}$ |
| 400 | $16 \times 10^{68}$ |
| 500 | $32 \times 10^{45}$ |
| 600 | $31 \times 10^{30}$ |
| 700 | $70 \times 10^{19}$ |
| 800 | $85 \times 10^{11}$ |
| 900 | $67 \times 10^{5}$ |

The large value of K indicates the reaction (1) should proceed easily to the right side if not kineticslly controlled. A confirmatory test for aluminum sulfate was carried out as follows.

0.2 gram of the reaction product were dissolved in 100 ml water and then the solution was concentrated to 50 ml by evaporation. The solution was further filtered to remove undissolved solid.

(1) Detection of Sulfate

10 ml of the filtered solution was neutralized with a drop of 10 % sodium hydroxide solution. About 0.5 ml of 6 % barium chloride solution was added. The appearance of a finely divided white precipitate confirmed the formation sulfate.

### (2) Detection of Aluminum

10 ml of sample solution was mixed with sodium hydroxide solution. The appearance of white precipitate, $AL(OH)_3$, indicated that aluminum ion was present.

## C. PARAMETER EVALUATION

### (1) Time

Sulfation reaction is very fast on the time scale of this experiment for an $SO_2$ concentration of 8,352 ppm and an $O_3$ concentration of 39,400 ppm. Therefore, Sample weighing was taken over a short time interval, 30 sec. & 1 min.. This will give a smooth data curve of % conversion vs. time and % absorption vs. time.

### (2) Temperature

A wide range of operating temperature was used in this study. The temperatures were adjusted by controlling the percentage volt output of the variable transformer. The following datum give relationship between % volt output and temperature.

| % Volt Output | Temperature ($^{\circ}C$) |
|---|---|
| 30 | 194 |
| 40 | 275 |
| 45 | 350 |
| 50 | 407 |
| 55 | 468 |
| 60 | 520 |
| 70 | 640 |
| 80 | 730 |

### (3) Particle Size

Three different particle sizes were used : 0.3175 cm, 0.0833 cm, & 0.0495 cm. These were obtained by crushing 1/8 inch alumina balls and followed by classfication using standard sieves.

(4) Alumina Sample Weight

Between 0.15 to 0.2 gram of alumina sample was used in each experimental run. This range of weight was determined by trial and error to avoid 100 % absorption of $SO_2$ in the first 30 sec..

(5) Gas Flow Rate

In this study, $O_2$ was always in excess. The flow of $O_2/O_3$ was within the range 0.015 cfm-0.16 cfm (at 8 psig, 70°F) and would provide a range of velocity from 1.11 m/sec.- 11.84 m/sec.. Over this range a negligible effect of gas flow on the sulfation was observed, indicating that the rate of sorption was not limited by mass transfer to solid surface (18).

(6) $SO_2$ Concentration

$$\text{The concentration of } SO_2 = \frac{\text{Flow Rate of } SO_2 \text{ (in standard cond.)}}{\text{Flow Rate of } O_2/O_3 \text{(in standard cond.)}}$$

However, the flow rate of $O_2/O_3$ was measured in 70°F, and 8 psig. Therefore, it was necessary to convert the flow rate to standard condition (32°F, 1 atm),

1 sccm = 0.7 ccm at 8 psig and 70°F

1.4 sccm = 1 ccm at 8 psig and 70°F

Where, sccm stands for standard cubic centimeter per minute at STP.

$$SO_2 \text{ concentration} = \frac{V_{SO_2}/5 \times 100 \times 0.69 \text{ (sccm)}}{Q_{O_2/O_3} \times 28,316.84 \times 0.7 \text{ (sccm)}} \times 10^6$$

Where the flow rate of $SO_2$ = $V_{SO_2}$ / 5 X 100 X 0.69 (4)
( sccm )

$V_{SO_2}$ = the reading of the mass flow meter

$Q_{O_2/O_3}$ = the flow rate ( CFM ) of $O_2/O_3$ at 70°F, 8 psig

1 CFM = 28316,84 ccm

(7) Residence Time ( $\tau$ )

Residence time is calculated by the following equation

$$Q_T = Q_{O_2/O_3} \times 28316.84 + V_{SO_2} / 5 \times 100 \times 0.69 \times 1.41$$

Where $Q_T$ = total flow rate of $O_2/O_3$ and $SO_2$ streams
( ccm at 8 psig, 70 °F )

$$\tau = \frac{W_s / 3.1 \times \varepsilon / ( 1-\varepsilon )}{Q_T} \qquad (5)$$

Where $W_s$ = Weight of Sample

$\varepsilon$ = Frational void of the packed. bed.

3.1 = Specific Gravity of Alumina ( TABLE 1 )

$\tau$ = Residence time.

(8) Ozone Concentration

Variation in gas flow rate, gas pressure, voltage, temperature, , cooling water flow rate.will affect the concentration of ozone generated . Therefore, throughout the experiment, all conditions were kept as constant as possible at 8 psig, 70 °F and 5 gallon per hour water flow rate.

The ozone concentration at different gas flow rates and voltages were calibrated by passing the ozonized gas through a 100 ml of 2 percent solution of neutral potassium iodide in 2 minutes. Ozone reacts with potassium iodide solution according to the reaction,

$$H_2O + 2KI + O_3 \rightarrow O_2 + I_2 + 2KOH \qquad (6)$$

However, $I_2$ will react further with KOH as follows

$$3I_2 + 6KOH \longrightarrow KIO_3 + 5KI + 3H_2O \qquad (7)$$

Therefore, the resulting solution is acidified with 1 M sulfuric acid to decompose iodate and liberate iodine,

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3H_2O + 3I_2 \qquad (8)$$

Then the iodine is titrated with standardized 0.1 N sodium thiosulfate solution according to the reaction

$$2S_2O_3^= + I_2 \longrightarrow 2I^- + S_4O_6^= \qquad (9)$$

A total of thirty -one test runs were obtained, basically at six flow rates with different electrical power inputs. The result of all these tests is summarized in ( TABLE 2 , and FIGURE 5 and 6 )

(9) Percentage Conversion (Accumulated)

The % conversion of $AL_2O_3$ to $AL_2(SO_4)_3$ was caculated according to the following equations:

$$a = M_1 X_{10} \qquad (10)$$

$$b = M_1 X_1 + M_2 X_2 \qquad (11)$$

Where a = Weight of Solid, at time 0

b = Weight of Solid, at time t

$X_{10}$ = Number of moles of $AL_2O_3$ at time 0

$X_1$ = Number of moles of $AL_2O_3$ at time t

$X_2$ = Number of moles of $AL_2(SO_4)_3$ at time t

$M_2$ = Molecular Weight of $AL_2(SO_4)_3$

TABLE 2. SUMMARY OF OZONE GENERATION TESTS

| (cfm) FLOW RATE \ VOLT | | 115 | 105 | 95 | 85 | 75 | 55 |
|---|---|---|---|---|---|---|---|
| 0.015 | a | 39,367 | 35,612 | 31,493 | 29,071 | 26,890 | 10,295 |
| | b | 2.34 | 2.11 | 1.87 | 1.728 | 1.59 | 0.612 |
| 0.040 | a | 27,254 | 26,799 | 24,074 | 20,168 | 14,717 | |
| | b | 4.32 | 4.248 | 3.81 | 3.196 | 2.33 | |
| 0.070 | a | 22,322 | 21,024 | 18,532 | 14,120 | 10,174 | |
| | b | 6.192 | 5.832 | 5.14 | 3.196 | 2.82 | |
| 0.100 | a | 16,534 | 15,698 | 13,154 | 9,884 | 7,522 | |
| | b | 6.55 | 6.22 | 5.21 | 3.916 | 2.98 | |
| 0.130 | a | 13,557 | 12,159 | 9,559 | 7,687 | 5,870 | |
| | b | 6.89 | 6.26 | 4.92 | 3.96 | 3.02 | |
| 0.160 | a | 11,174 | 9,470 | 7,949 | 6,291 | 4,769 | |
| | b | 7.08 | 6.00 | 5.04 | 3.98 | 3.024 | |

a : ppm ( by volume ) of $O_3$ , at 70°F, 8 psig

b : gram per hour

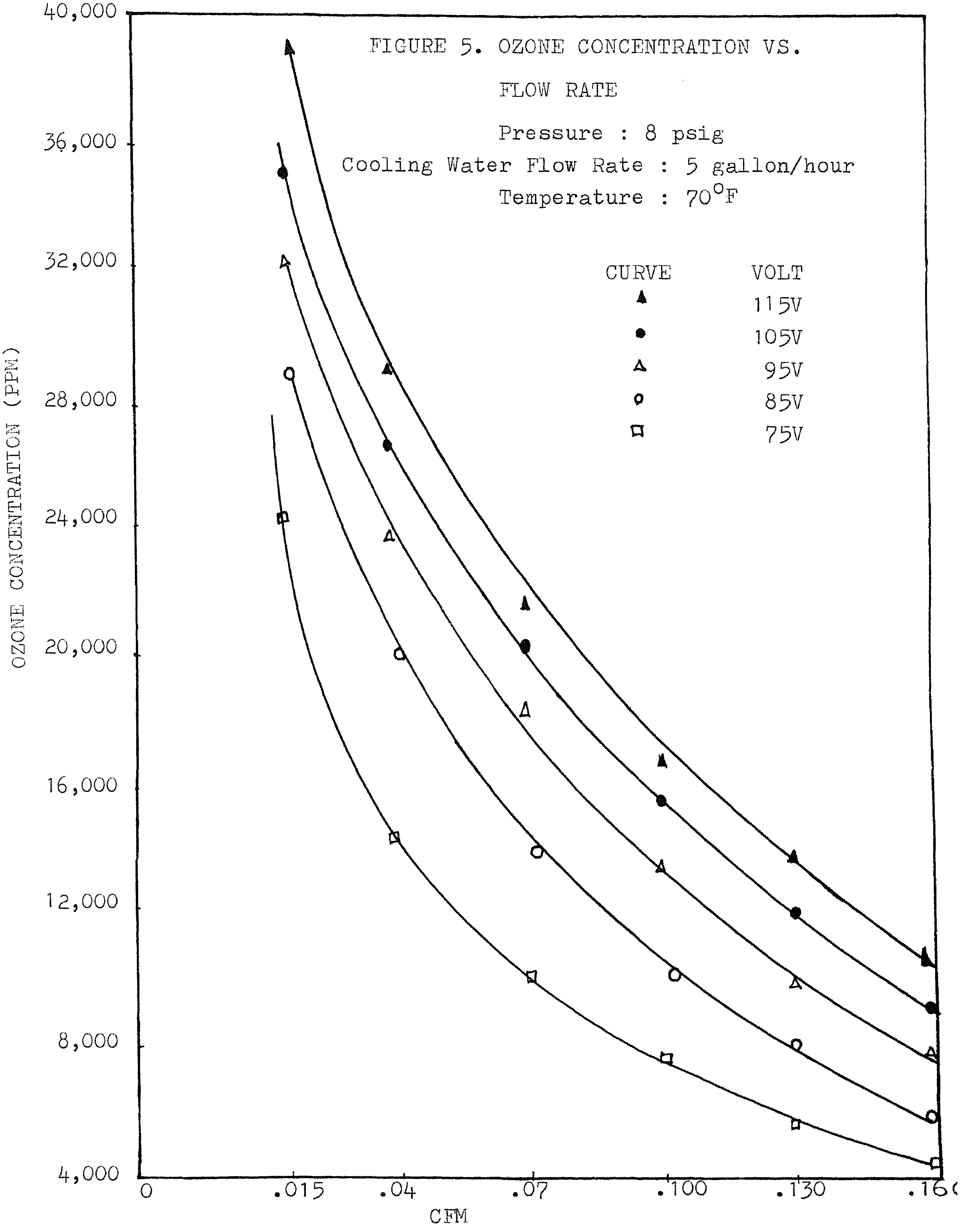


FIGURE 5. OZONE CONCENTRATION VS. FLOW RATE

Pressure : 8 psig
Cooling Water Flow Rate : 5 gallon/hour
Temperature : 70°F

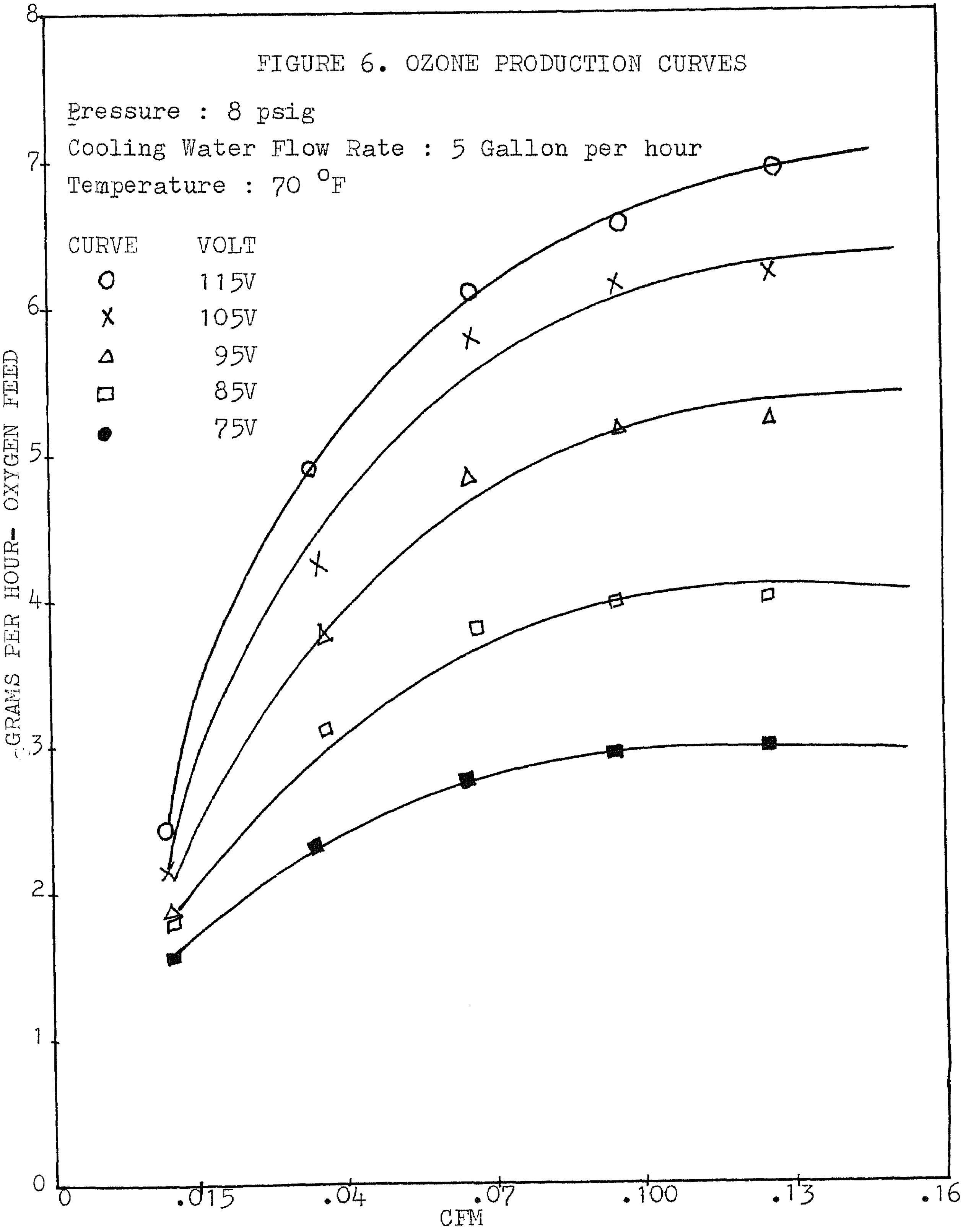


FIGURE 6. OZONE PRODUCTION CURVES

$M_1$ = Molecular Weight of $AL_2O_3$

Then, $X_{10} = X_1 + X_2$ (12)

the accumulated conversion of $AL_2O_3 = \frac{X_2}{X_{10}}$

$$= \frac{b-a}{a}\left( \frac{M_1}{M_2 - M_1} \right) \quad (13)$$

$$\% \text{ conversion} = \frac{b-a}{a} \times 42.4527$$

(10) Percentage Absorption

Percentage absorption of $SO_2$ per gram of $AL_2O_3$

$$= \frac{SO_2 \text{ absorbed by } AL_2O_3 \text{ to form } AL_2(SO_4)_3}{\text{molar flow rate of } SO_2 \times t_c} \quad (14)$$

According to equation (1), three moles of $SO_2$ was absrbed to form one mole of $AL_2(SO_4)$. % absorption

$$\text{of } SO_2 = \frac{3X_2}{F_{SO_2} \times t_c} \quad (15)$$

Where $F_{SO_2}$ = molar flow rate of $SO_2$

$= V_{SO_2}/5 \times 100 \times 0.69 \times \frac{1}{22,400}$

$t_c$ = Contact Time of $SO_2$ with Solid ( min. )

From equation(13),

$X_2 = X_{10} \times$ Conversion

$= a/M_1 \times$ ( % Conversion ) $\times \frac{1}{100}$ (16)

and set a = 1 gram

Therefore, % absorption of $SO_2$ per gram of $AL_2O_3$

$$= \frac{3 \times 1/M_1 \times ( \% \text{ Conversion} ) \times 22{,}400}{V_{SO_2}/5 \times 100 \times 0.69 \times t_c}$$

$$= \frac{\% \text{ Conversion}}{V_{SO_2} \times t_c} \times 47.77 \qquad (17)$$

D. PROCEDURE

A. To perform a sulfation run, the following steps were conducted:

1. The furnace temperature was set at the desired temperature by adjusting the transformer output.
2. All the valves were closed, and the circuit breaker of the ozonator was placed in off position.
3. The mass flow meter was turned on.
4. Alumina samples were placed in the quartz ( or pyrex ) tube reactor.
5. The reactor was inserted into furnace and connected to the system.
6. Valve 6 was opened letting $O_2$ in to dry the sample for 20 min., then valve 6 was closed. ( about 0.015 cfm )
7. The reactor was disconnected from the system, suspended to the weighing pan of the balance ( FIGURE 2 ), and the weight of the reactor was noted.
8. Steps 5 to 7 were repeated until there was no change reactor weight.
9. Valve V6 was opened for 1 min. and then closed. Next valves V3 and V5 were opened and the pressure regulator of the ozonator was adjusted to 8 psig.
10. (i) If sulfation with UV irradiation was conducted, the UV lamp was inserted into furnace and the lamp

power wasturned on.

(ii) If sulfation run with ozone was conducted, cooling water was started through the ozonator, the circuit breaker switch was set at on position, and the voltage was adjusted to give the desired reading on voltmeter.

(iii) If UV light or ozone was not invoved, this step was skipped.

11. Valve V2 was opened and the metering valve V1 was adjusted to give the desired reading on the mass flow meter for 1 min. ( or 30 sec. ).

12. Valves V2, V5, and V3 were the closed ( to prevent excessive pressure within the ozonator), and valve V6 was opened for 1 min. to purge the reactor with $O_2$.

13. (i) For sulfation with ozone, voltage of the ozonator was reduced to zero.

    (ii) For sulfation with UV, the lamp power was switched off.

    (iii) If UV or ozone was not involved, this step was skipped.

14. Valve V6 was closed and the reactor was disconnected from the system and weighed.

15. The reactor was reassembled and steps 9 to 14 were repeated until no appreciable weight increase was measured in a reasonable period of time.

B. To perform ozone concentration test runs, the following steps were conducted.

1. Valves V2, V4, V6, and V5 were closed, while sample valve ( on the panel of ozonator, shown in FIGURE 3 ) and valve V3 were opened, and the voltage and flow rate were adjusted to desired valve.
2. The sample valve was closed and valve V4 was opened. The $O_2/O_3$ stream was diverted into a disperser containing KI solution.

# EXPERIMENTAL RESULT AND DISCUSSION

The progress of the sulfation reaction with time under various condition was recorded using a balance. The data are presented in TABLE 3 through TABLE 19. In this investigation, three different experiments were conducted:

(i) Sulfation with oxygen/ozone.

(ii) Sulfation with oxygen only in the presence of UV radiation. Two different wave lengths of UV, 254 nm and 366 nm, were used.

(iii) Sulfation with oxygen only.

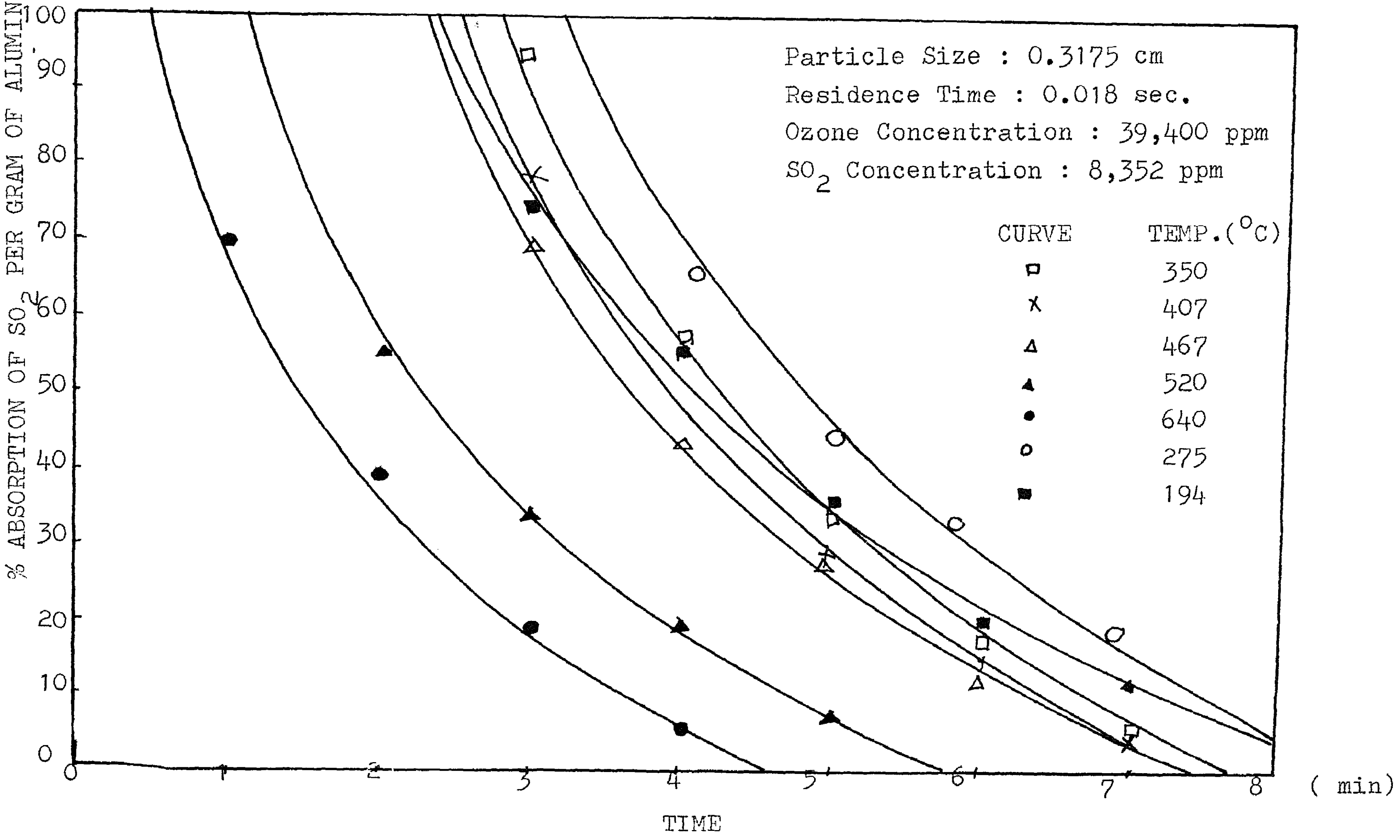
In each experiment , runs were carried at various temperature, residence time, $SO_2$ inlet concentration, and particle size.

- SULFATION WITH OXYGEN / OZONE.

- Temperature

The effect of temperature on the reaction is shown in FIGURE 7. The adsorption of $SO_2$ increased with temperature up to about 275°C and then decreased. As shown in FIGURE 7, at 275°C the $SO_2$ was completely absorbed in the first 3 min. and absorption became negligibly small after 8 minutes. For temperature above 520°C, the $SO_2$ was completely absorbed in the first 1 min., and absorption then became zero after 6 min. From the study of ozone oxidation of $SO_2$ in the flue gas by Slatter

FIGURE 7. TIME-ABSORPTION DATA ( SULFATION WITH OXYGEN/OZONE )



Particle Size : 0.3175 cm

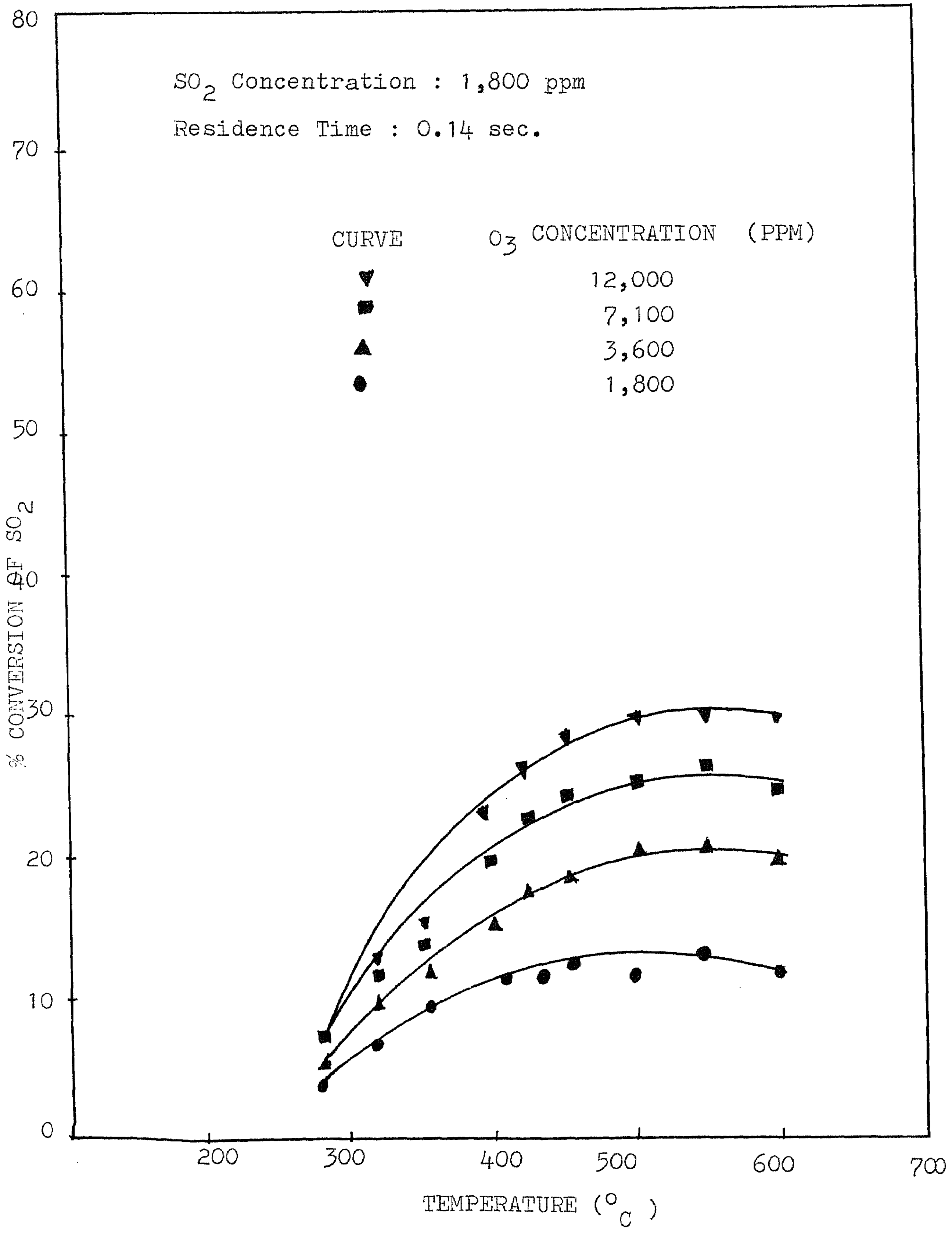
Residence Time : 0.018 sec.

Ozone Concentration : 39,400 ppm

$SO_2$ Concentration : 8,352 ppm

FIGURE 8. CONVERSION VS. TEMPERATURE

( DATA EXCERPTED FROM SLATTER AND RIZZON )



& Rizzon (14) , they reported that the conversion of $SO_2$ to $SO_3$ by $O_3$ increased with temperature up to 550 °C and then decreased ( as shown in FIGURE 8 ), and the conversion increased monotonically with ozone concentration. Thus , it is expected that the presence of ozone should promote the absorption of $SO_2$ by alumina, because $SO_3$ is much more reactive than $SO_2$ .

- $SO_2$ Concentration

In FIGURE 9, the % conversion of alumina to aluminum sulfate is shown to increase with increasing $SO_2$ concentration. After a period of about 5 minutes, it begins to level off, indicating a gradual reduction in reactivity of the particles. The same set of data were re-plotted in terms of % absorption of $SO_2$ vs. time in FIGURE 10. At low $SO_2$ inlet concentration, complete absorption of $SO_2$ prevails over a longer period of time before it begins to drop. As $SO_2$ inlet concentration increases, absorption of $SO_2$ starts to decrease from 100% sooner. Thus, from these two figures ( FIG. 9 & 10 ) ,we can deduce that absorption of $SO_2$ is very rapid initially with fresh alumina particles and as reaction proceeds the aluminum sulfate formed appears to close some of the pores in the particles. Eventually , most of the pores are closed and mass transfer resistance

FIGURE 9. TIME -CONVERSION DATA (SULFATION WITH OXYGEN / OZONE )

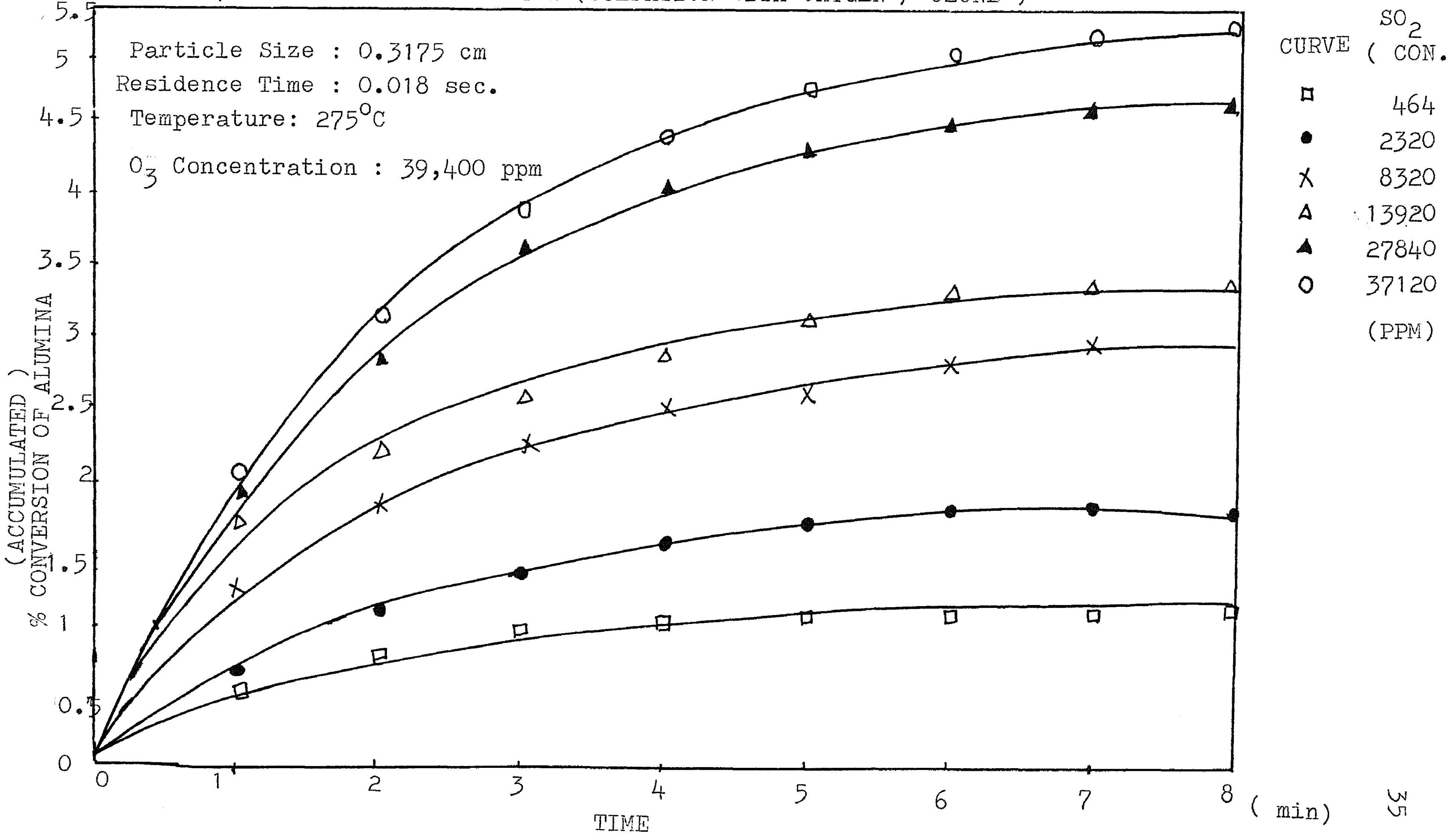
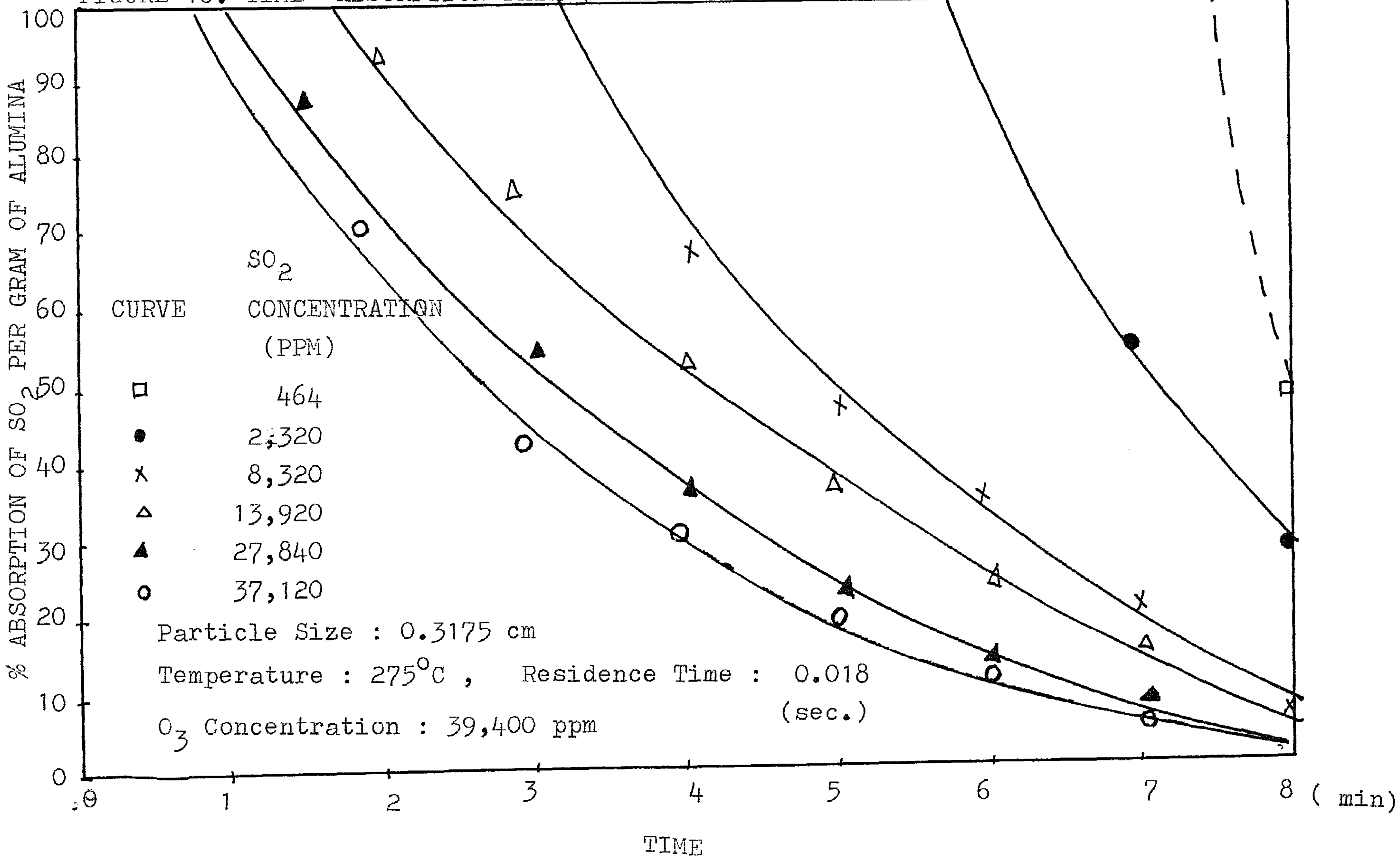


FIGURE 10. TIME -ABSORPTION DATA ( SULFATION WITH OXYGEN / OZONE)



through the product layers drastically increases resulting in retardation of gas-solid reaction. Slatter and Rizzone (14) observed that at a given temperature, residence time and ozone concentration , the % conversion of $SO_2$ to $SO_3$ decreased slightly as the inlet concentration of $SO_2$ increased ( FIG. 11 ). However, it seems that this slight dependence of the conversion of $SO_2$ on $SO_2$ inlet concentration is inconsequential to the results as depicted in FIG. 9 and 10 .

- Residence Time

The absorption of $SO_2$ vs. time for several residence times is shown in FIG. 12. Within experimental errors, residence time seems to have no effect on the absorption of $SO_2$. ( except a small effects at extremes )

- Particle Size

The % absorption of $so_2$ vs. time for three particle sizes is shown in FIG. 13. The absorption capacity of the particles increases with smaller particle size, i.e. for a given amount of particles, smaller particles will absorb more $SO_2$ than larger particles over the period of time.

- Ozone Concentration

In Fig. 14, the % conversion of alumina is shown to increase from 1.8 % to 2.8 % as $O_3$ concentration

FIGURE 11. CONVERSION VS. $SO_2$ CONCENTRATION

( DATA EXCERPTED FROM SLATTER & RIZZON )

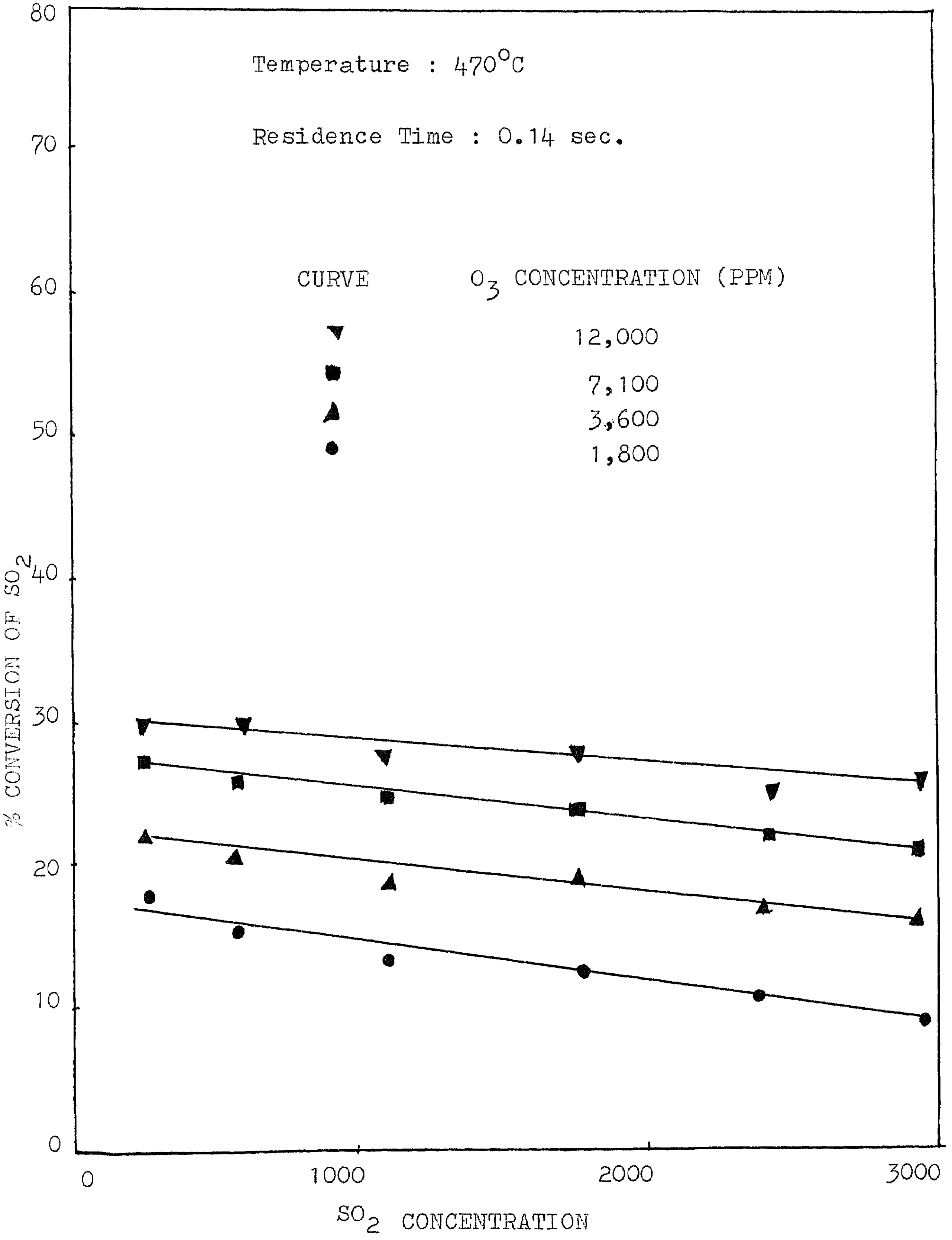


FIGURE 12. TIME - ABSORPTION DATA ( SULFATION WITH OXYGEN / OZONE )

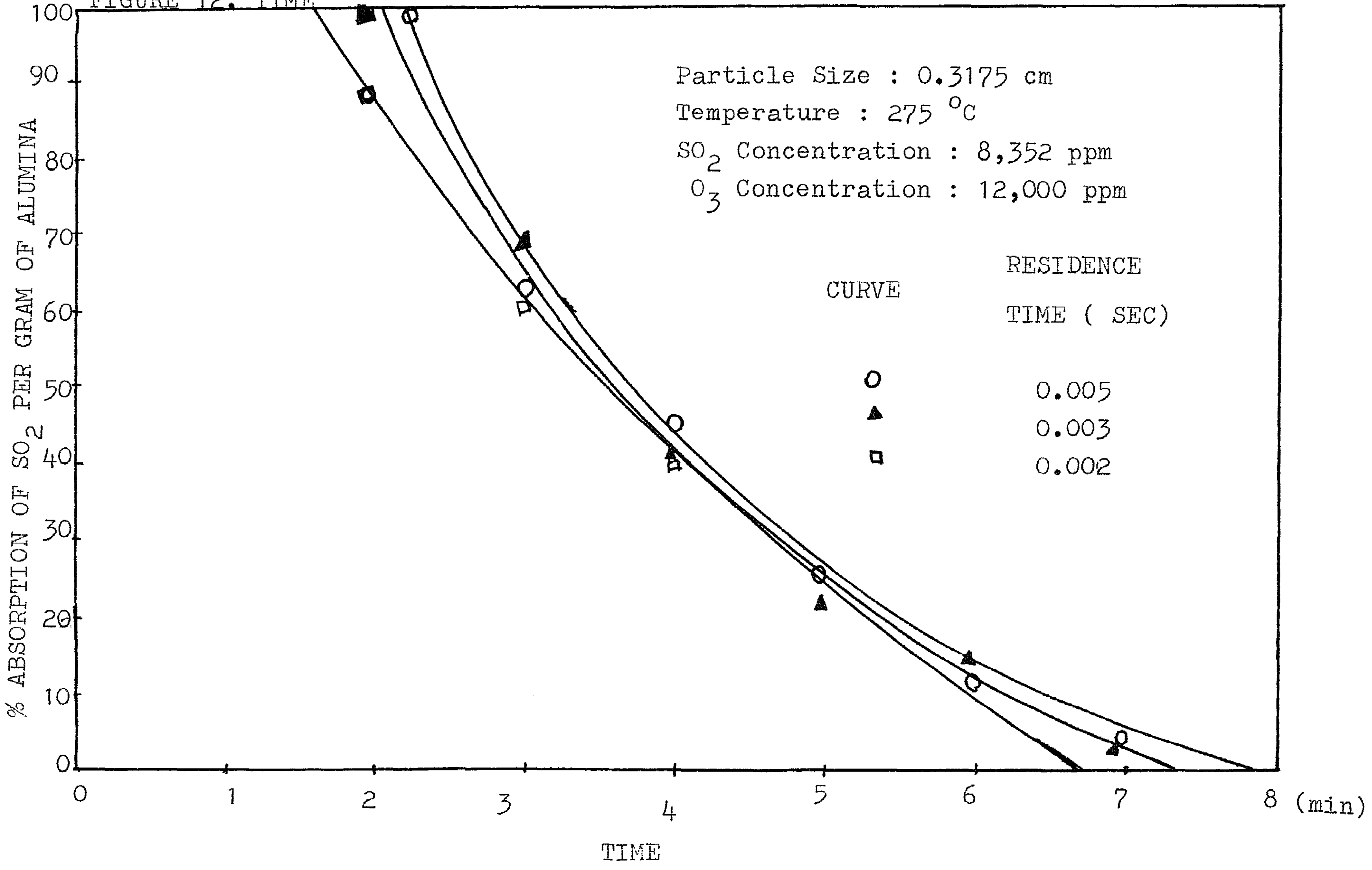
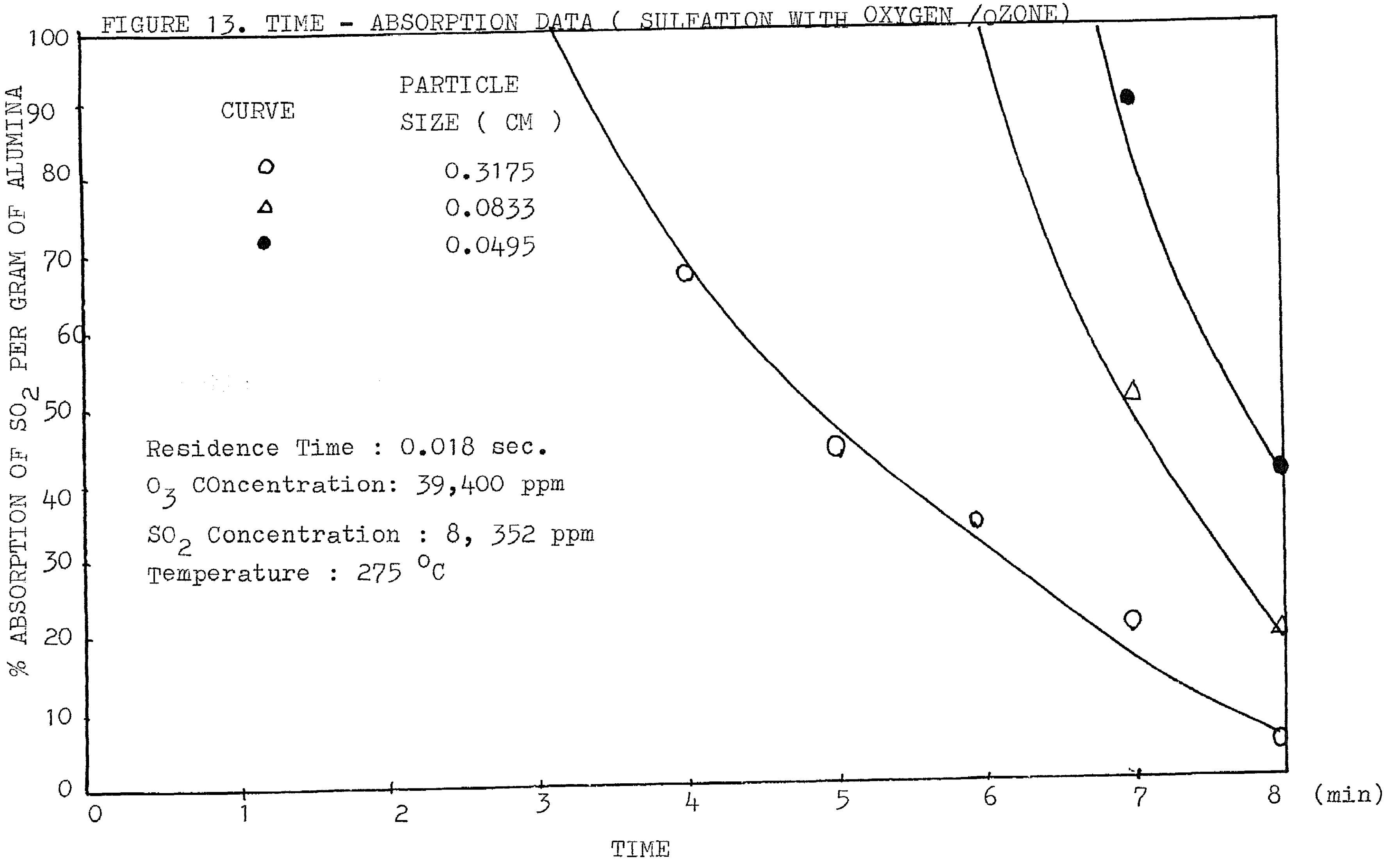


FIGURE 13. TIME - ABSORPTION DATA ( SULFATION WITH OXYGEN /OZONE)



Residence Time : 0.018 sec.
$O_3$ COncentration: 39,400 ppm
$SO_2$ Concentration : 8, 352 ppm
Temperature : 275 °C

( SULFATION WITH OXYGEN / OZONE )

FIGURE 14. OZONE CONCENTRATION- CONVERSION DATA

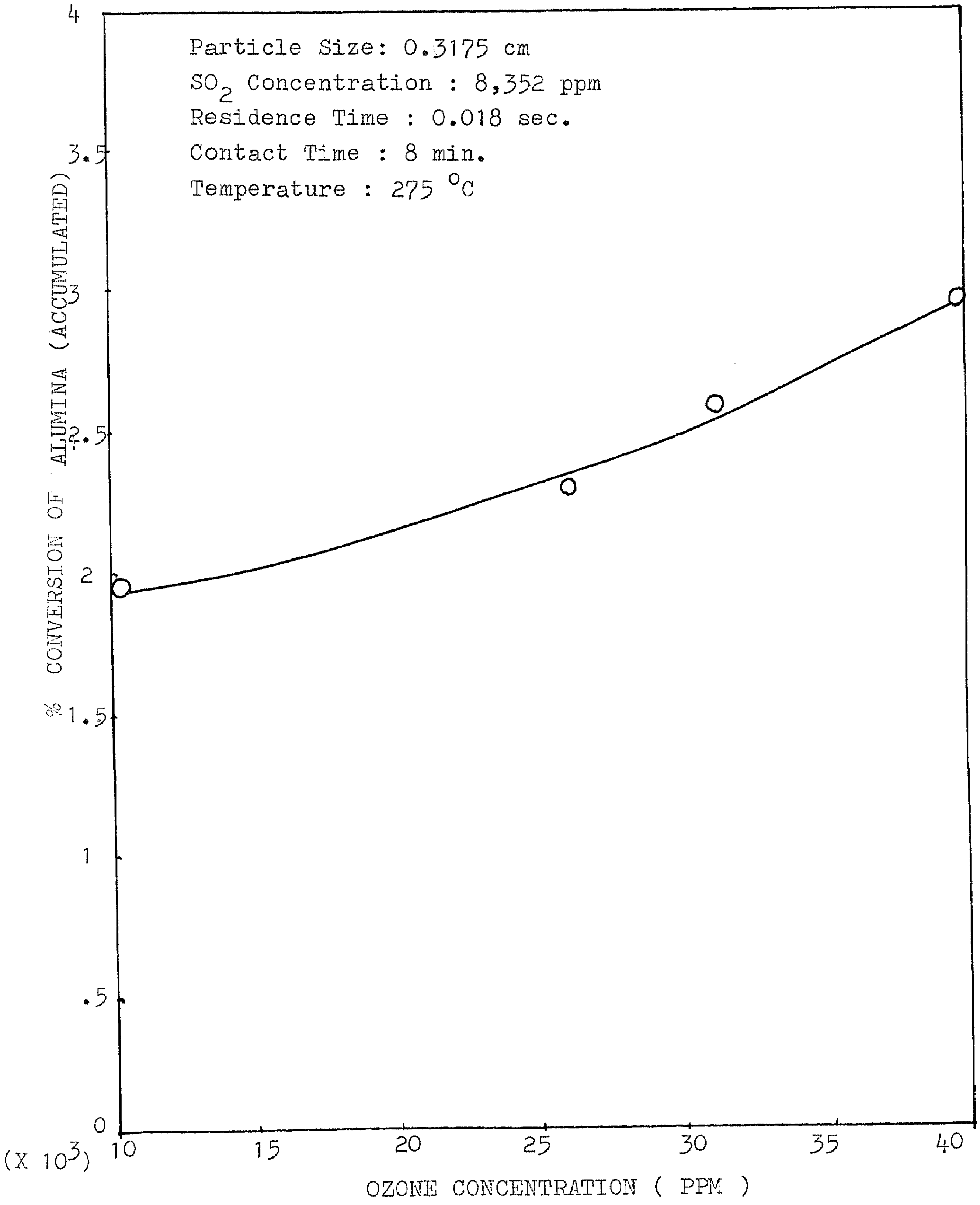
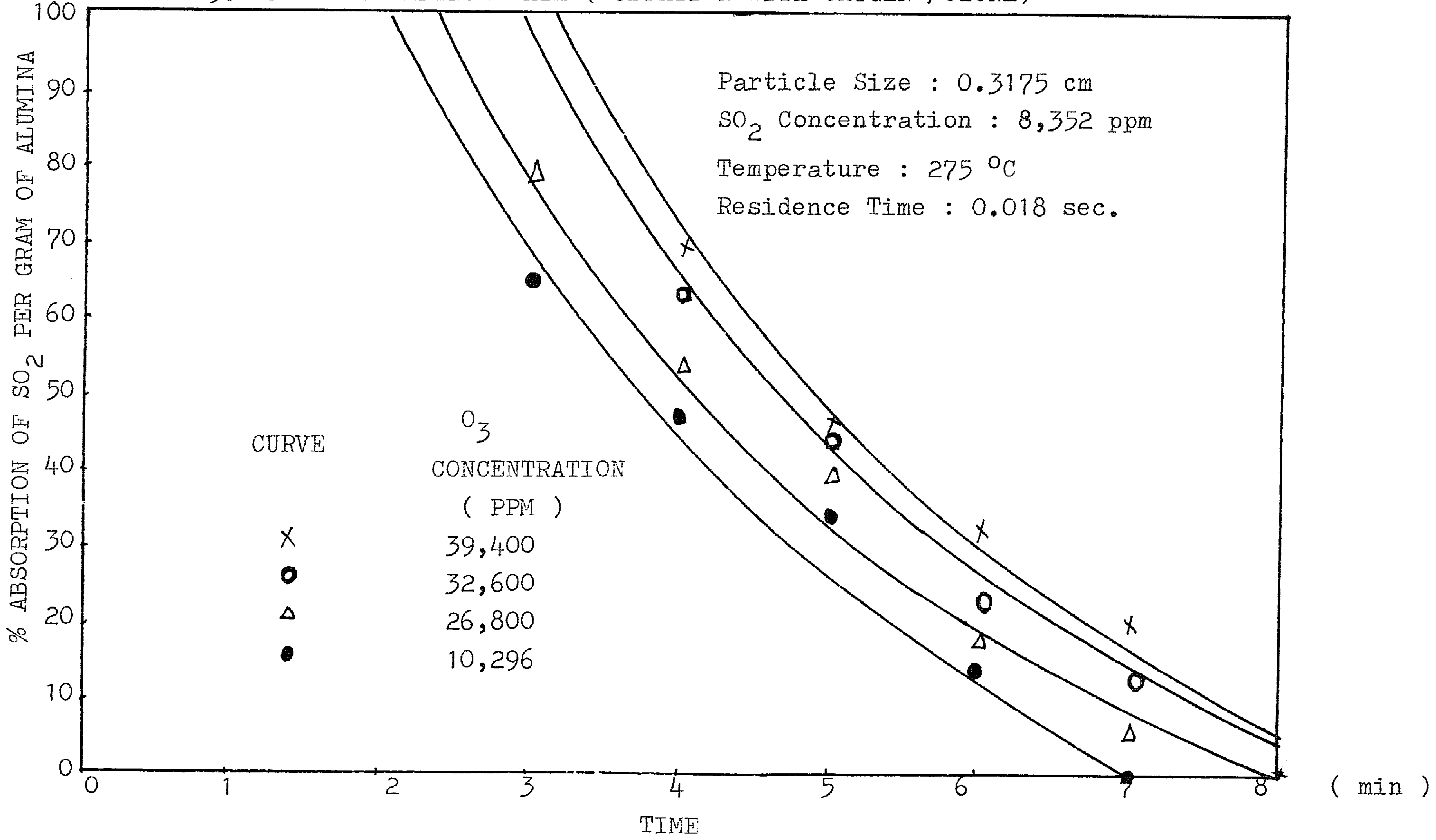


FIGURE 15. TIME -ABSORPTION DATA (SULFATION WITH OXYGEN /OZONE)



increased from 10,296 ppm to 39,400 ppm at 275°C. The same set of datum were re-plotted in FIGURE 15 in terms of % absorption of $SO_2$ vs. time. These two figures indicate that increased ozone concentration enchances sulfur dioxide absorption.

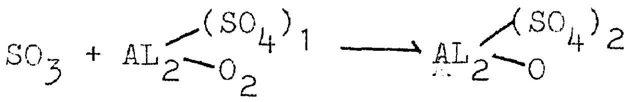
The proposed mechanism in this reaction is according to the following reactions,

$$SO_2 + O_3 \rightleftharpoons SO_3 + O_2 \qquad (18)$$

$$SO_2 + 02 \rightleftharpoons SO_3 + O \qquad (19)$$

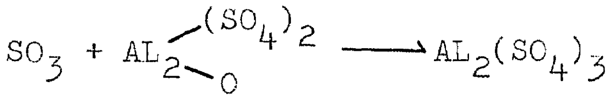
$$SO_3 + AL_2O_3 \longrightarrow AL_2{\substack{(SO_4)_1 \\ O_2}}$$

(20)



$$SO_3 + AL_2{\substack{(SO_4)_1 \\ O_2}} \longrightarrow AL_2{\substack{(SO_4)_2 \\ O}}$$

(21)



$$SO_3 + AL_2{\substack{(SO_4)_2 \\ O}} \longrightarrow AL_2(SO_4)_3$$

(22)

In the initial stage , say before 1 min., $SO_3$ was absorbed by $AL_2O_3$, and in order to maintain equilibrium between $SO_3$ and $SO_2$, the reaction 18 & 19 proceeds to the right side. Therefore, $SO_2$ was completely converted to $SO_3$, and then absorbed by $AL_2O_3$ particle to form $AL_2(SO_4)_3$.Because the molal volume $AL_2(SO_4)_3$ is larger than $AL_2O_3$, the formation of $AL_2(SO_4)_3$ form a more dense pore structure resulting in a decrease in porosity, which lead to pore-mouth closure, resulting incomplete conversion of $AL_2O_3$.

- SULFATION WITH OXYGEN ONLY , IN THE PRESENCE OF UV RADIATION.

(i) 254 nm UV radiation.

- Temperature

The % absorption of $SO_2$ increases with temperature up to 275 °C and DEcreases. ( FIG. 16 )

- $SO_2$ Concentration

The % absorption of $SO_2$ decreases with increasing of $SO_2$ inlet concentration. (FIG. 17 )

- Residence Time.

As shown in FIG. 18, residence time does not have much effect on absorption of $SO_2$.

- Particle Size

The % absorption of $SO_2$ increases with decreasing particle size of alumina. (FIG. 19 )

(ii) 366 nm UV light radiation

The % absorption of $SO_2$ vs. time at various temperature , $SO_2$ concentration, residence time, and particle size are shown in FIG. 20, 21, 22, and 23, respectively. The % absorption of $SO_2$ increases with temperature up to 275 °C and then decreases. The % absorption of $SO_2$ decreases with increasing $SO_2$ concentration, increases with increasing residence time and increases with decreasing particle size.

In general, the absorption characteristics of of alumina are similar for the two UV wavelenghs, 254 nm and 366nm, studied, although under identical conditions

FIGURE 16. TIME-ABSORPTION DATA ( SULFATION WITH $O_2$ ONLY IN THE PRESENCE OF UV)

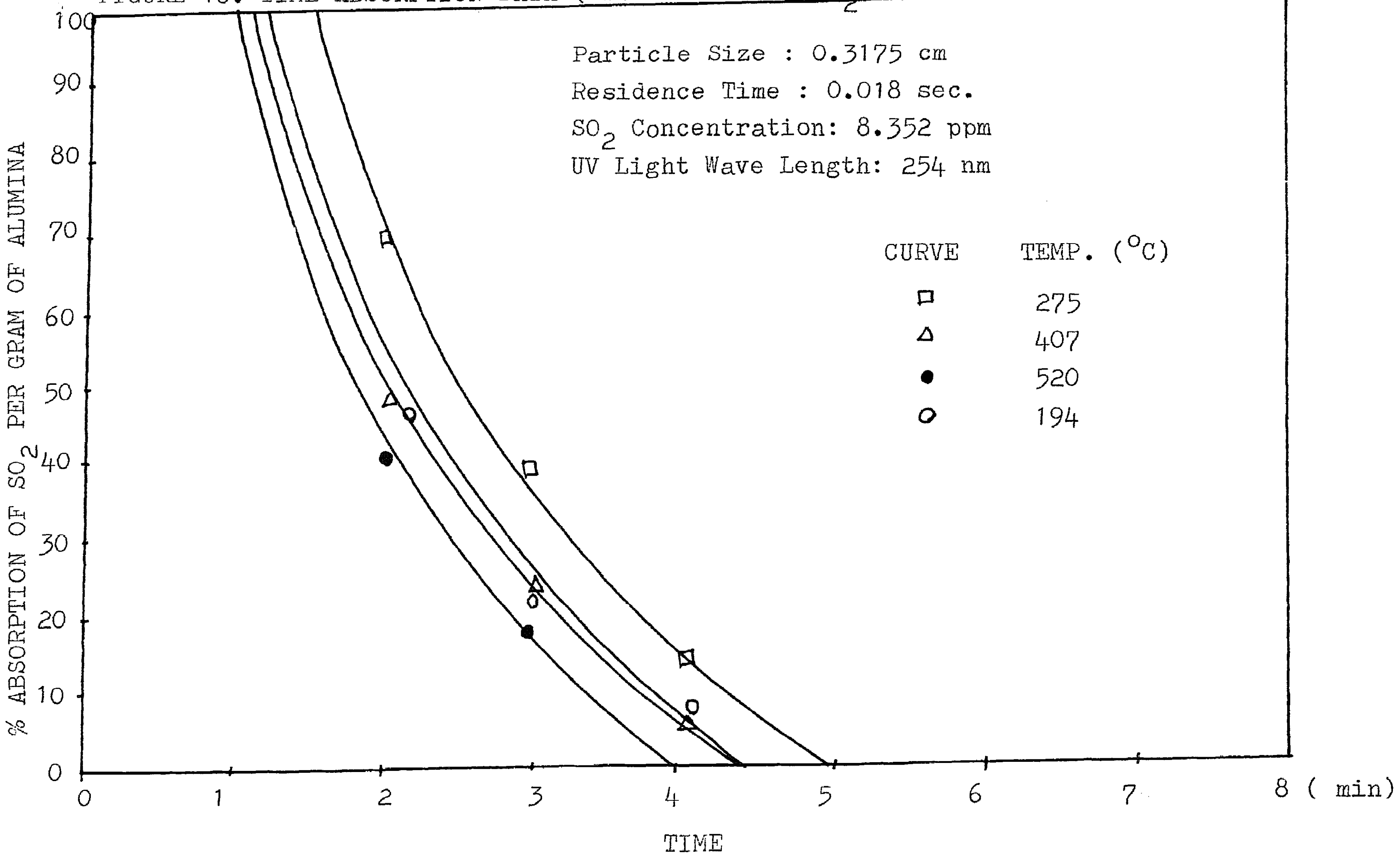


FIGURE 17. TIME-ABSORPTION DATA (SULFATION WITH $O_2$ ONLY IN THE PRESENCE OF UV)

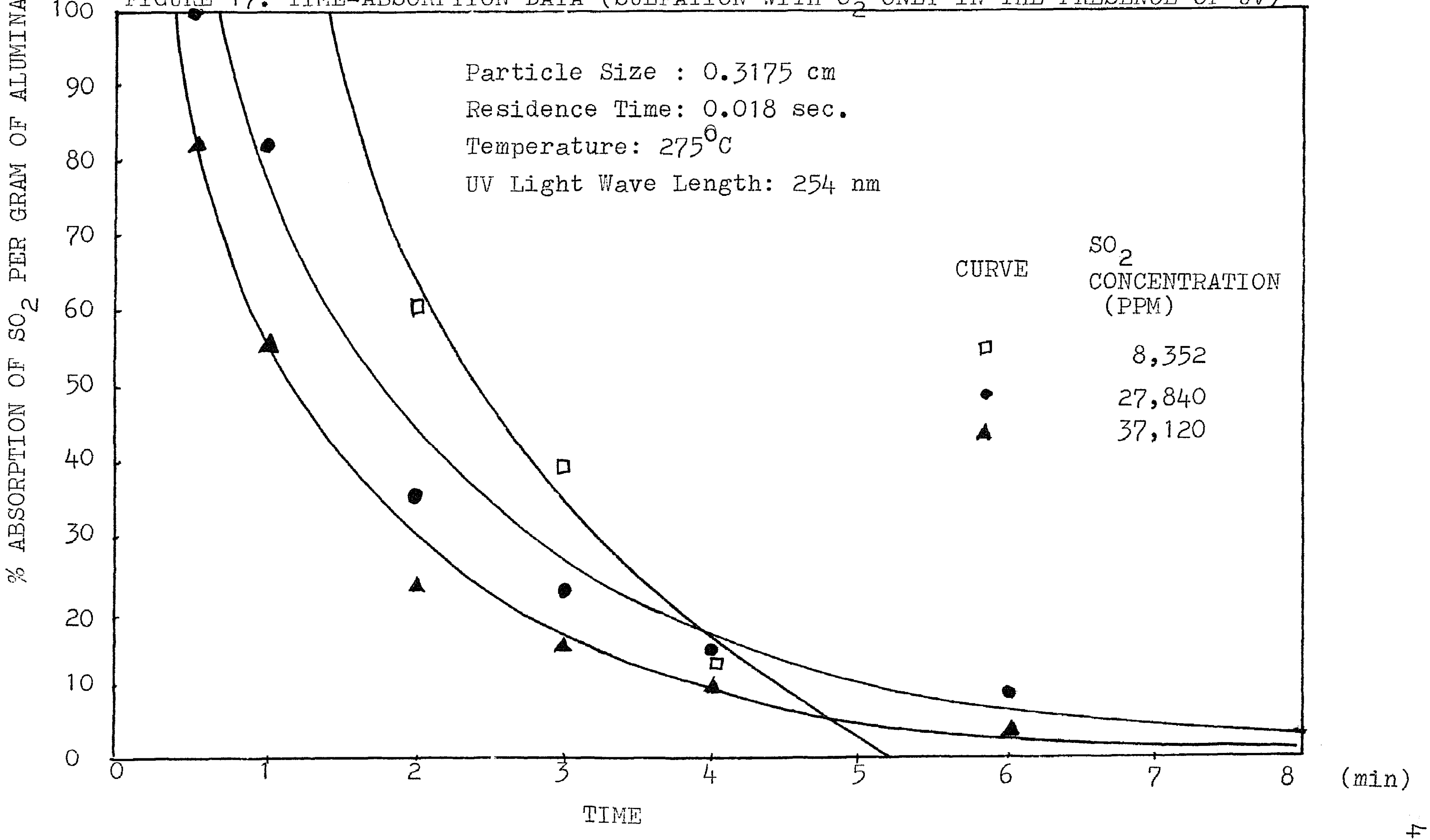

Particle Size : 0.3175 cm
Residence Time: 0.018 sec.
Temperature: 275 °C
UV Light Wave Length: 254 nm

FIGURE 18. TIME - ABSORPTION DATA ( SULFATION WITH $O_2$ IN THE PRESENCE OF UV RADIATION)

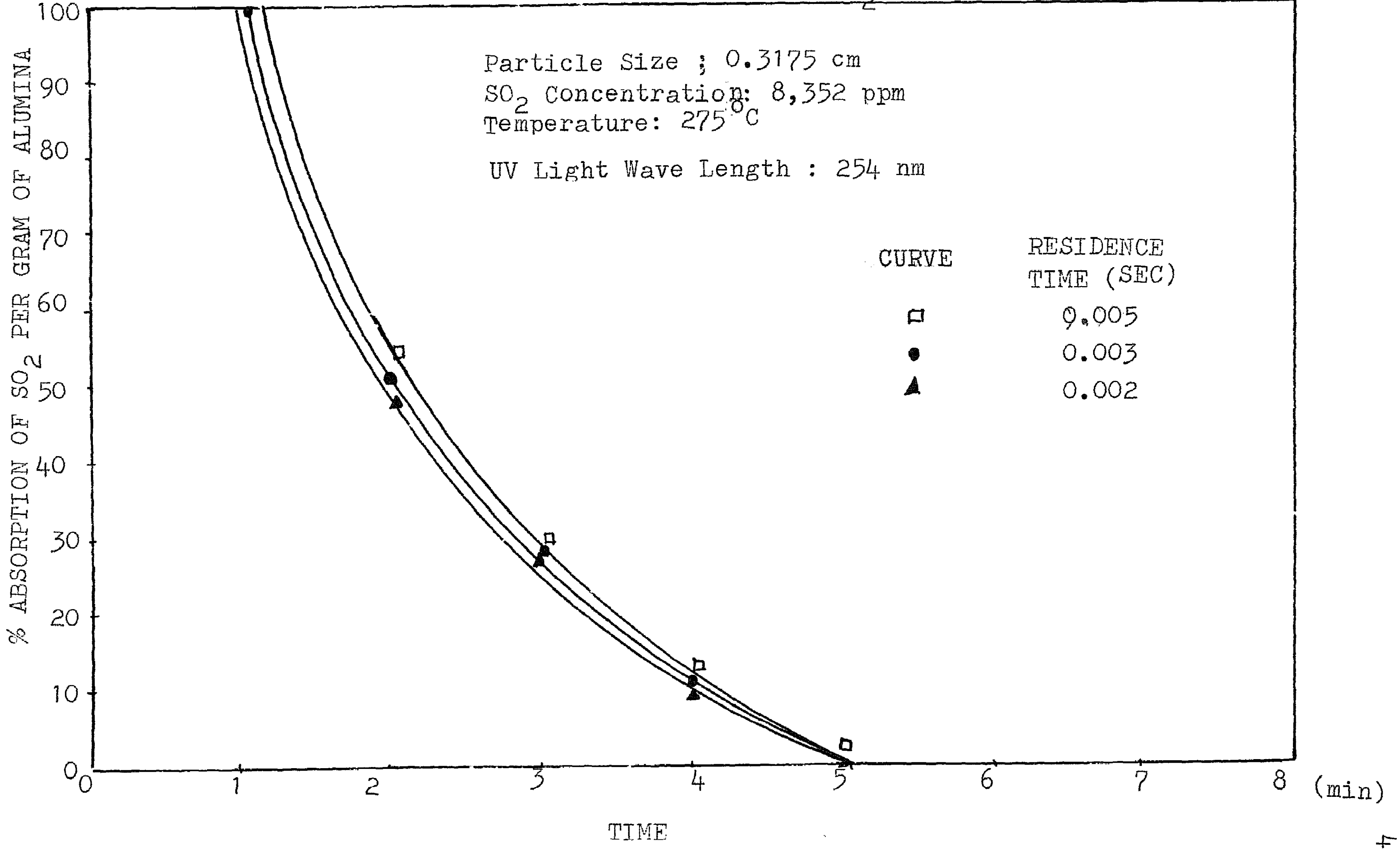
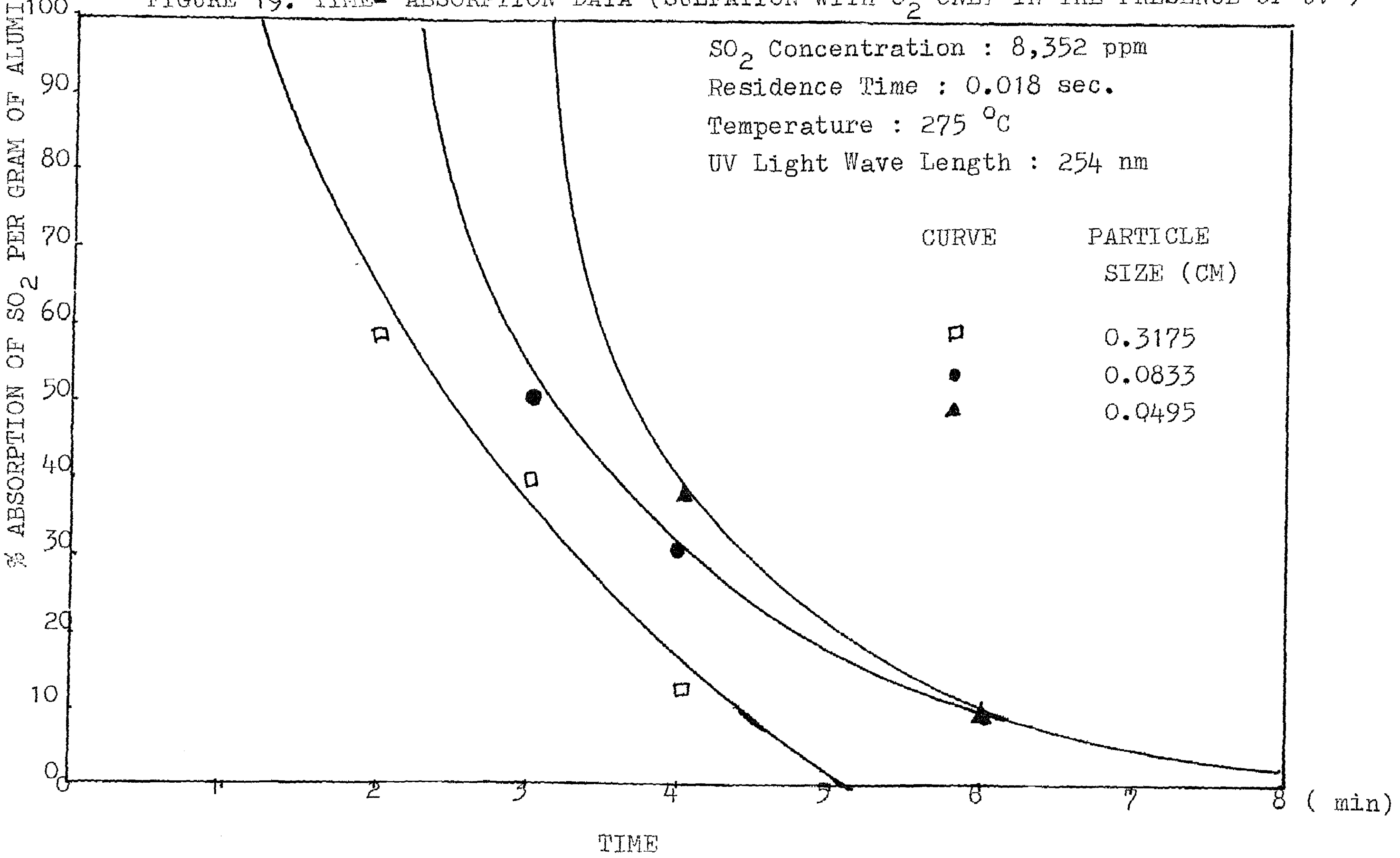


FIGURE 19. TIME- ABSORPTION DATA (SULFATION WITH $O_2$ ONLY IN THE PRESENCE OF UV )



$SO_2$ Concentration : 8,352 ppm
Residence Time : 0.018 sec.
Temperature : 275 °C
UV Light Wave Length : 254 nm

FIGURE 20. TIME- ABSORPTION DATA ( SULFATION WITH OXYGEN ONLY IN THE PRESENCE OF UV )

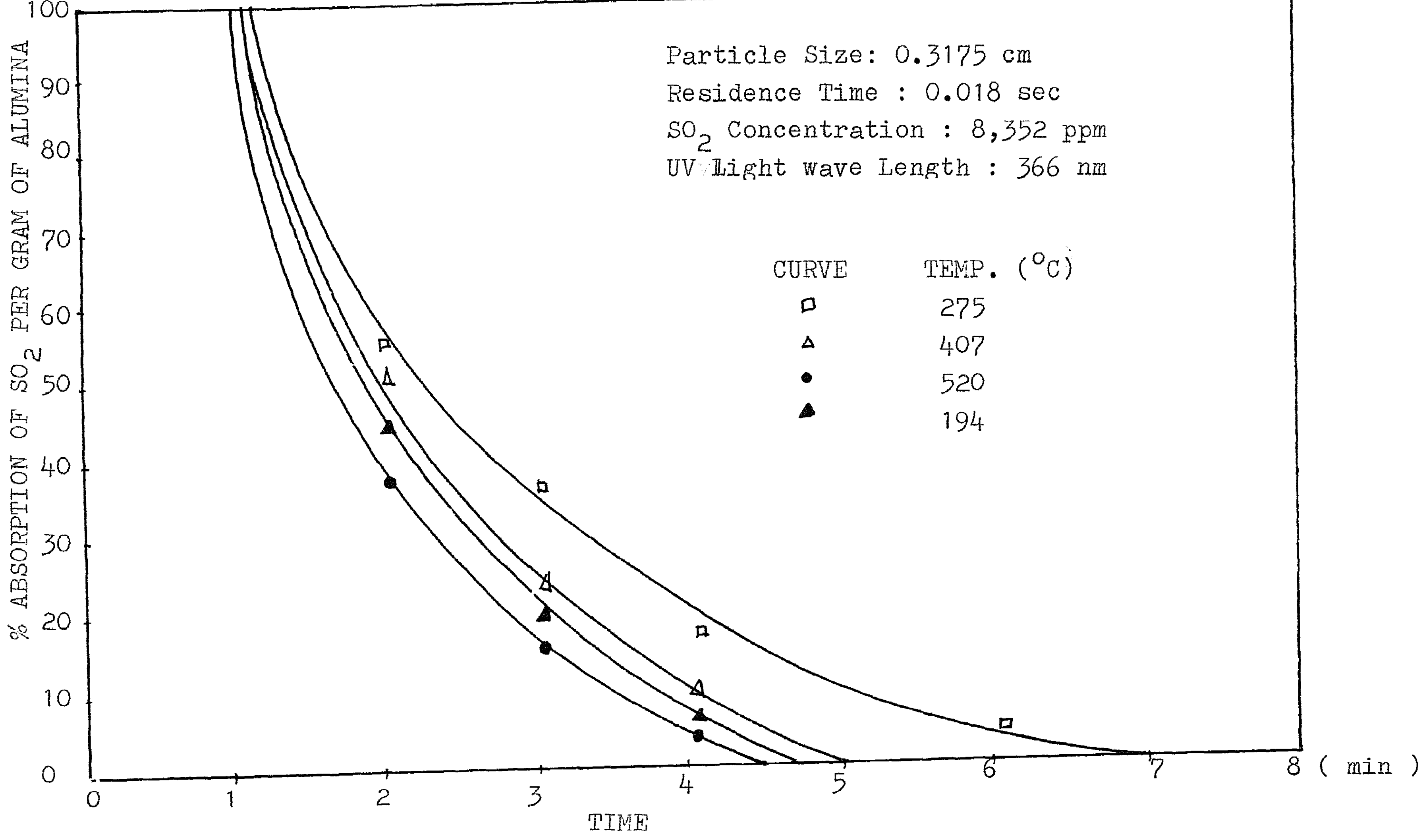


FIGURE 21. TIME- ABSORPTION DATA (SULFATION WITH $O_2$ IN THE PRESENCE OF UV RADIATION)

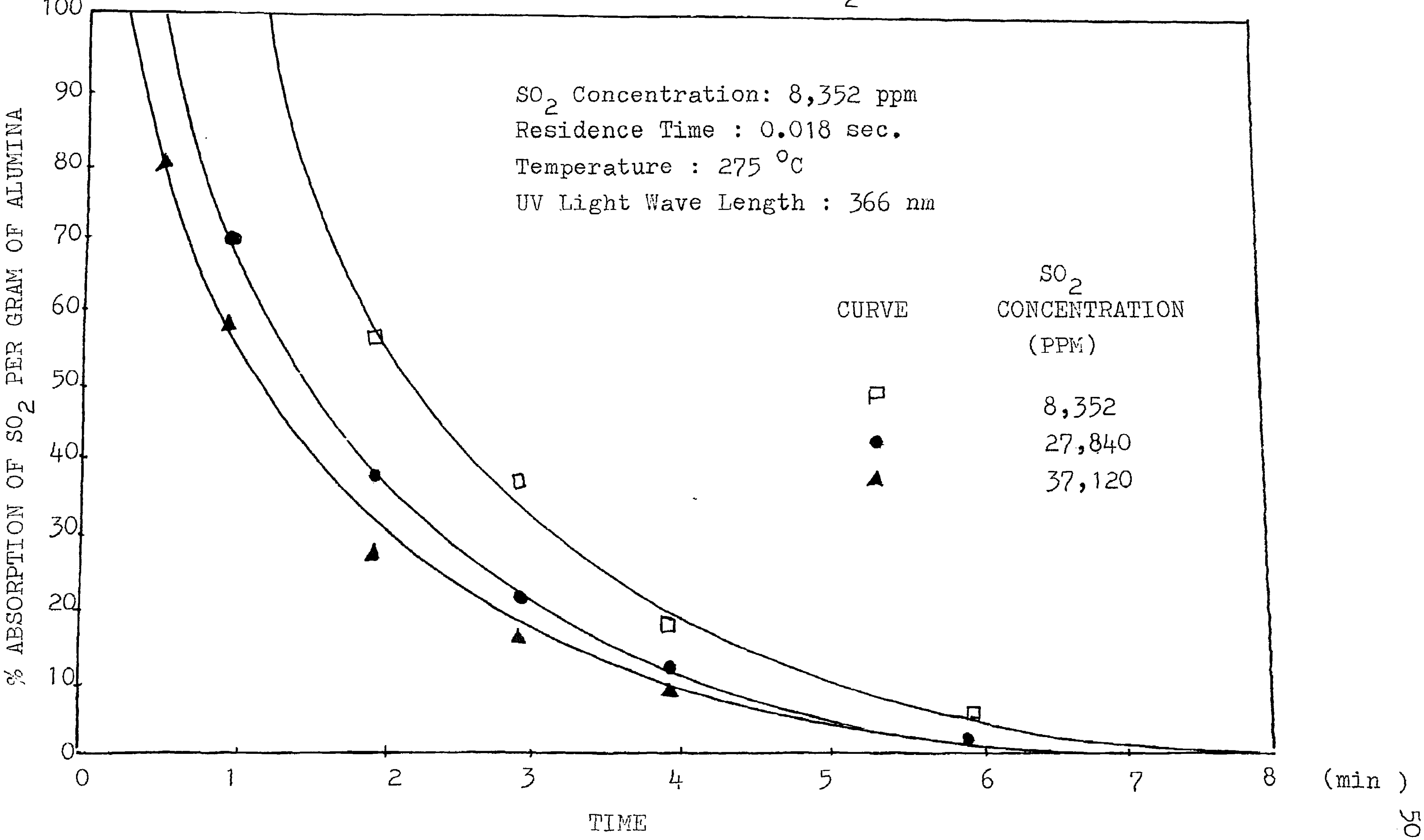


FIGURE 22. TIME-ABSORPTION DATA ( SULFATION WITH $O_2$ IN TH PRESENCE OF UV RADIATION)

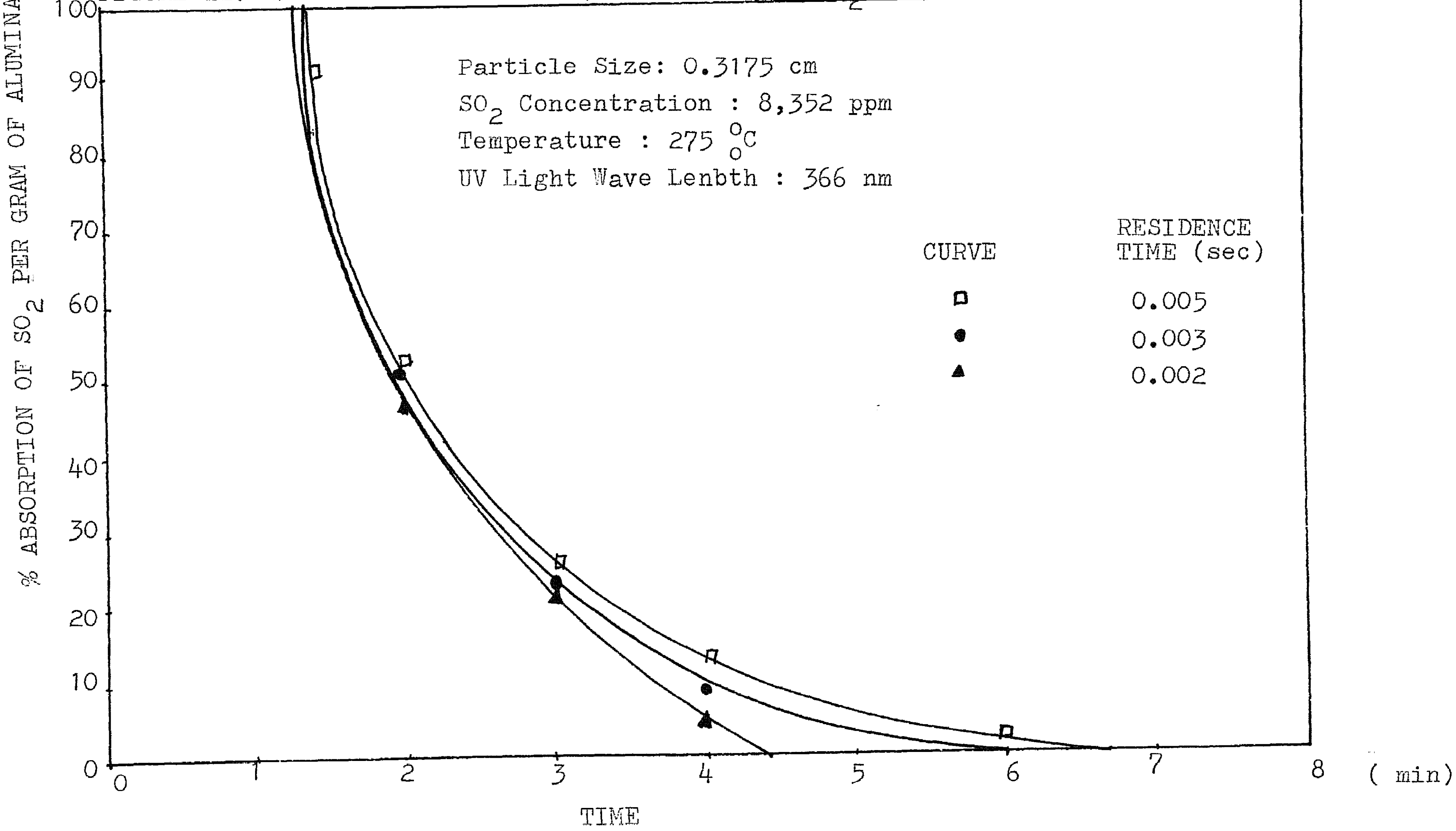
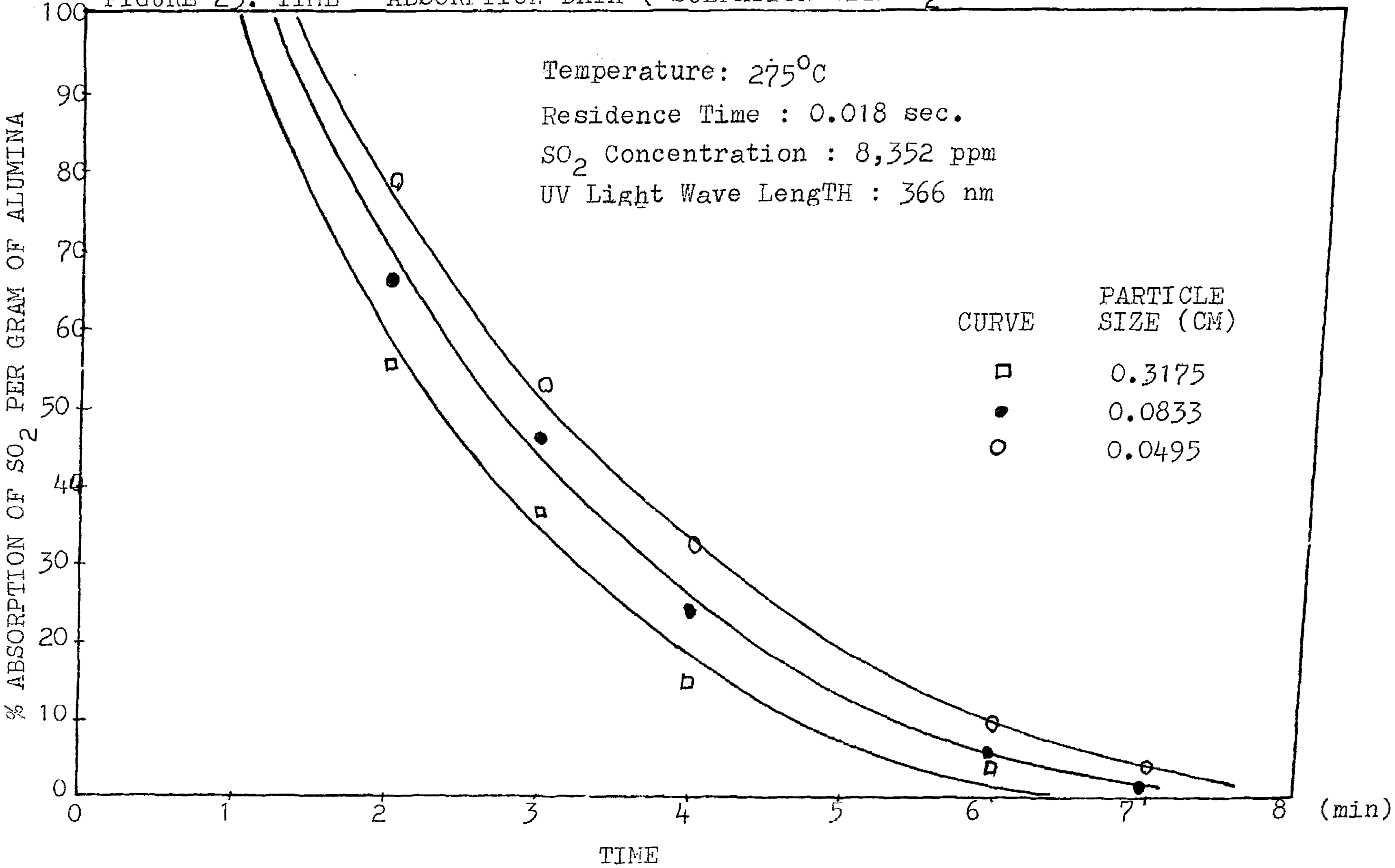


FIGURE 23. TIME - ABSORPTION DATA ( SULFATION WITH $O_2$ ONLY IN THE PRESENCE OF UV )



254 nm UV radiation induces slightly higher absorption.

- SULFATION WITH OXYGEN ONLY

- Temperature

The % absorption of $SO_2$ increases with temperature up to 640 °C and then decreases. ( FIG.24 )

- $SO_2$ Concentration

The % absorption of $SO_2$ decreases with increasing $SO_2$ concentration. (FIG 25)

- Residence Time

The % absorption increases with increasing residence time.(FIG.26 )

- Particle Size

The % absorption decreases with increasing particle size of alumina. (FIG. 27 )

In 1966, a paper by Culli, Hension (12) reported that, in the noncatalyzed gas phase reaction between $SO_2$ and $O_2$, the rate of formation of $SO_3$ was found to be $7.2 \times 10^{-6}$ mole liter$^{-1}$ min$^{-1}$ at 950°C. However, from FIG. 24, it is clear that % absorption of $SO_2$ was 100% in the first 30 sec. This demonstrates that the presence of $AL_2O_3$ seems to drive the reversible reaction

$$SO_2 + O_2 \rightleftharpoons SO_3 + O \qquad (19)$$

to the right by the formation of aluminum sulfate.

FIGURE 24. TIME-ABSORPTION DATA ( SULFATION WITH OXYGEN ONLY )

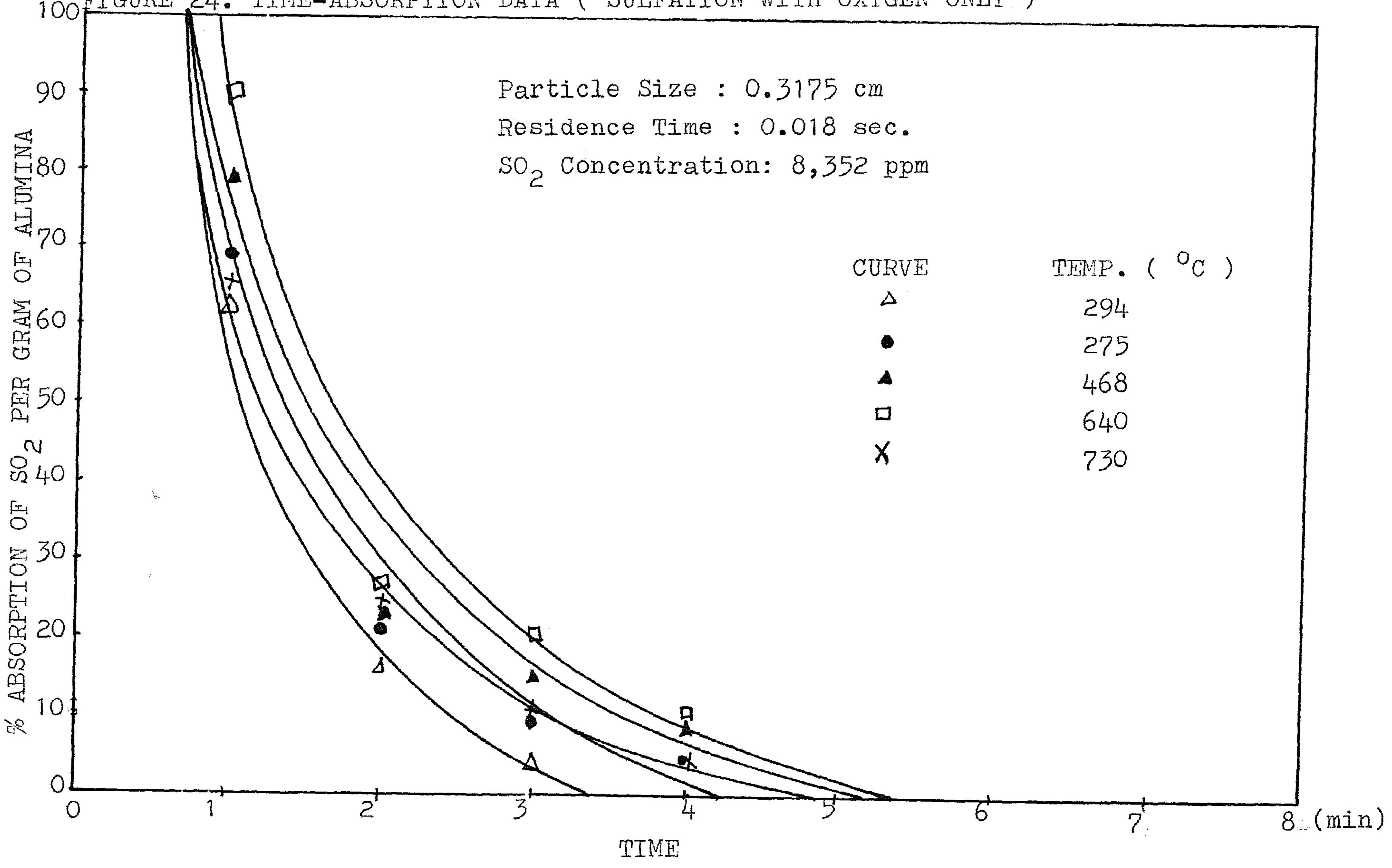


FIGURE 25. TIME - ABSORPTION DATA ( SULFATION WITH OXYGEN ONLY )

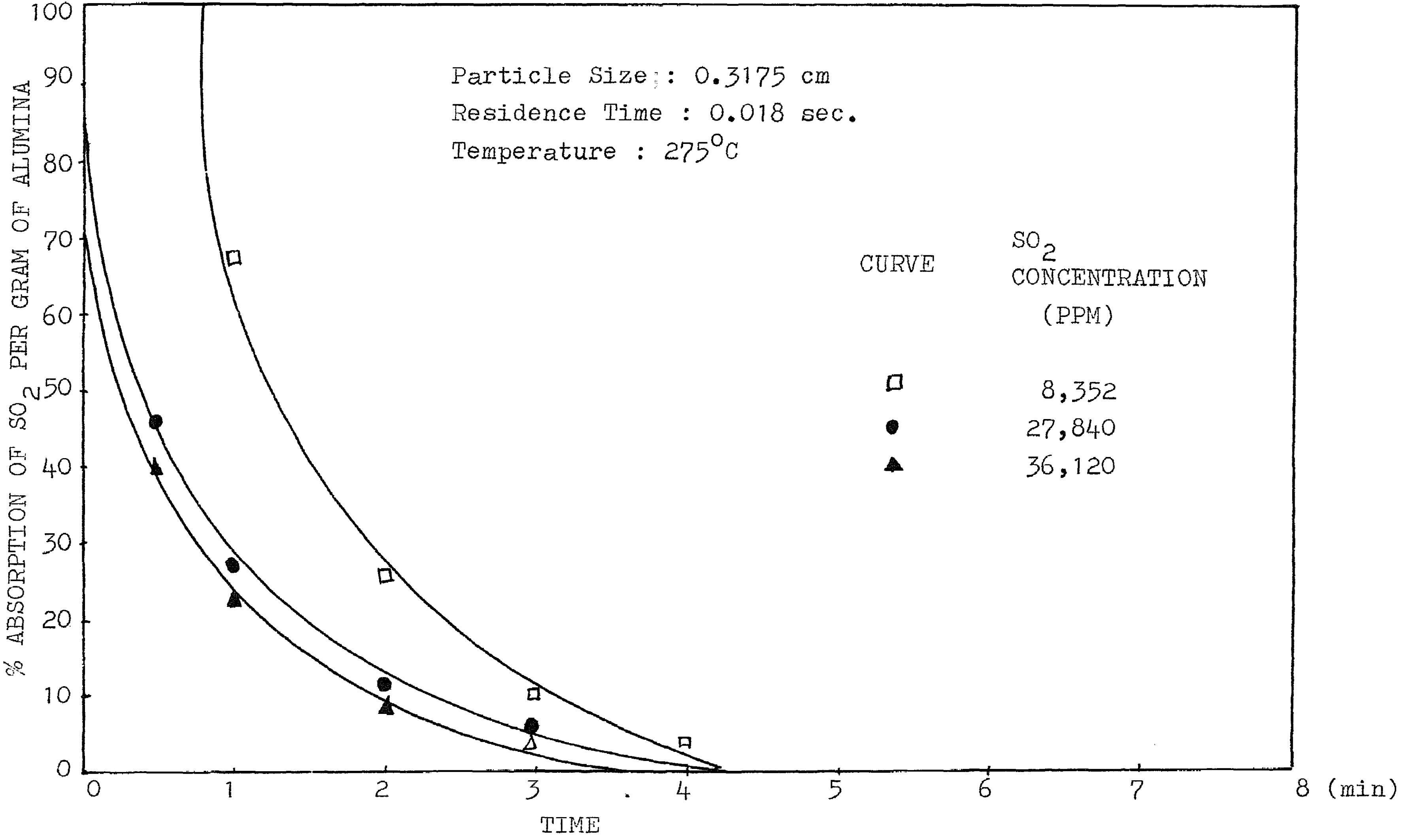


FIGURE 26. TIME -ABSORPTION DATA ( SULFATION WITH $O_2$ ONLY IN THE PRESENCE OF UV )

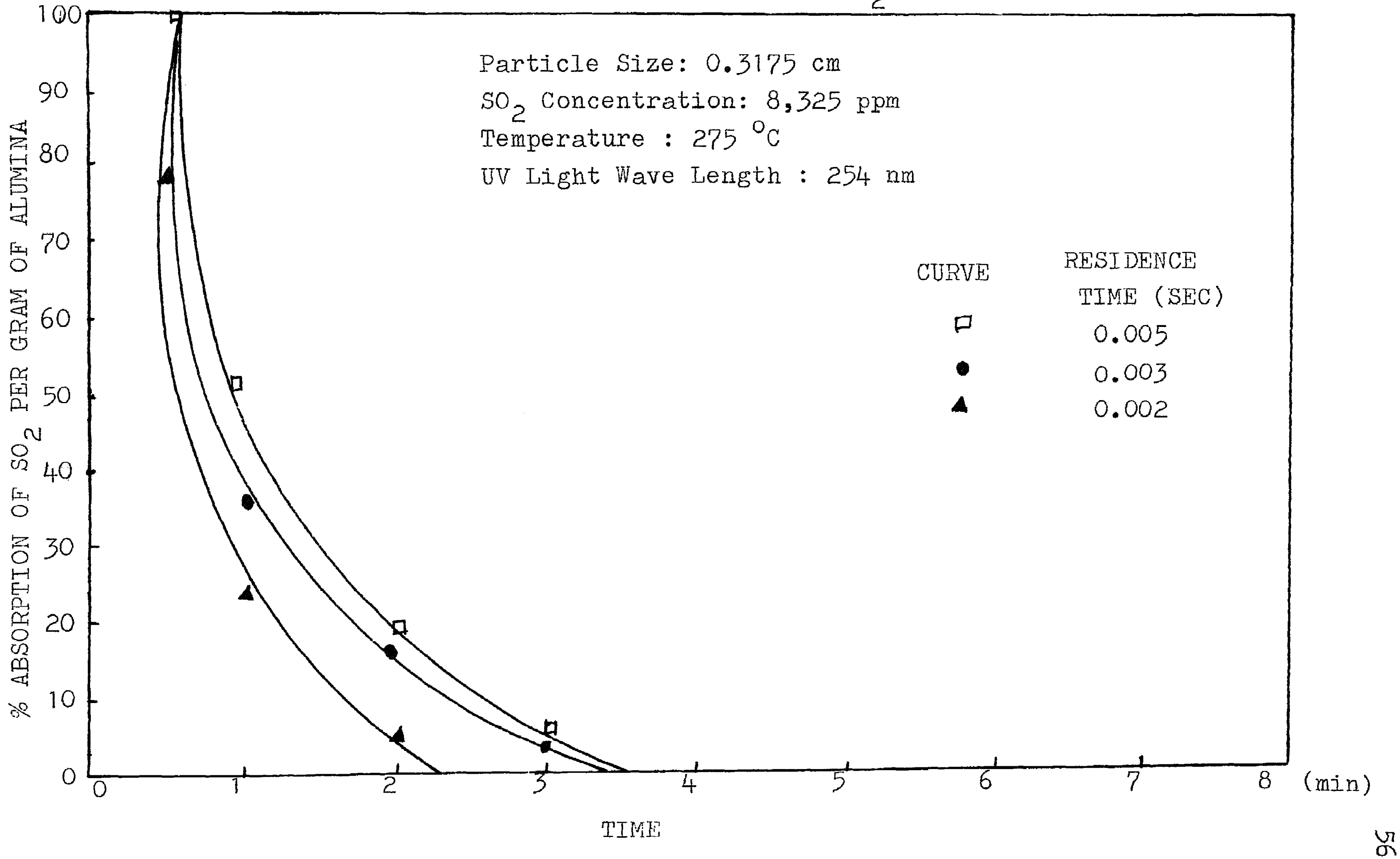
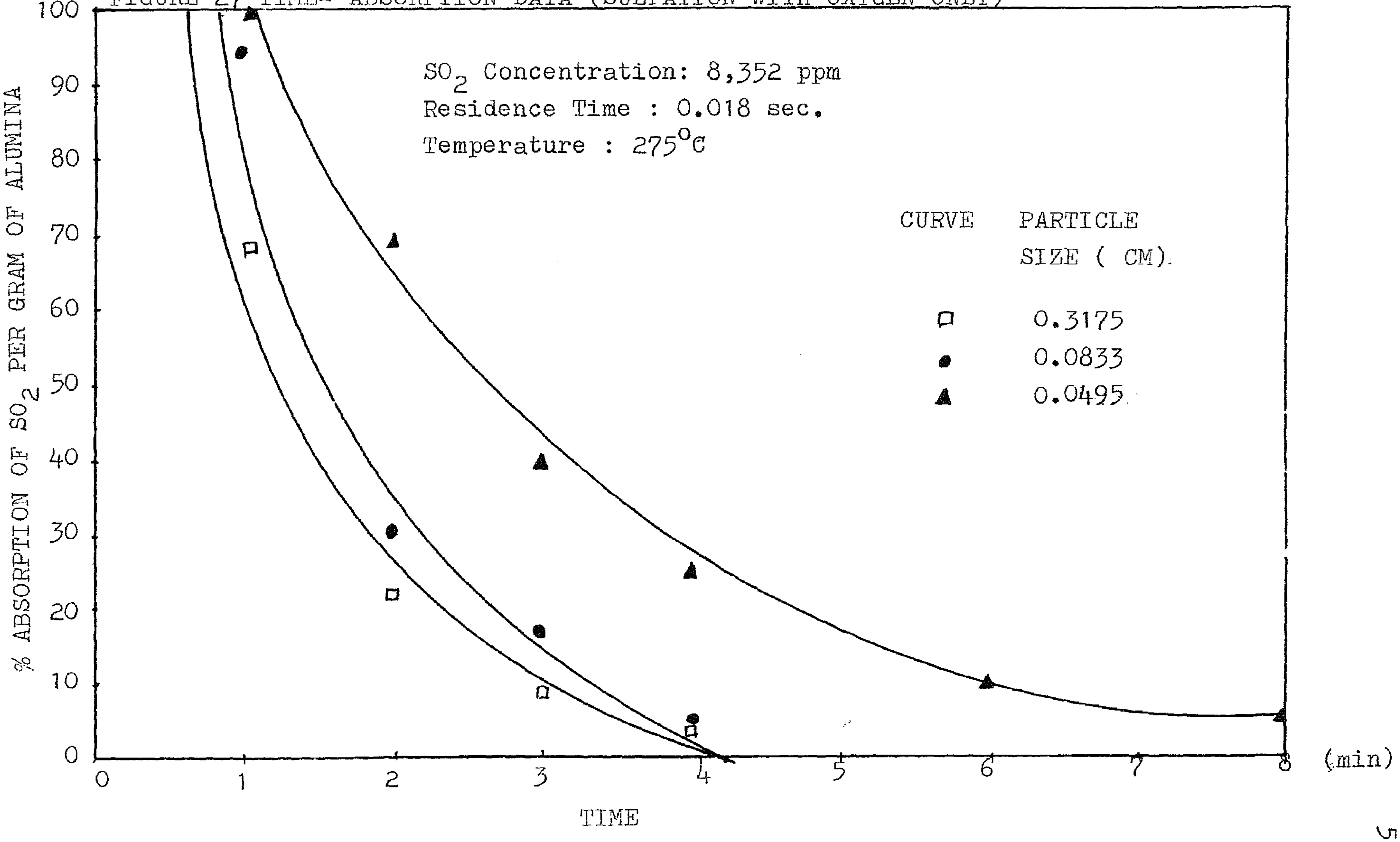


FIGURE 27 TIME- ABSORPTION DATA (SULFATION WITH OXYGEN ONLY)



In FIG. 28 to 31, the % conversion of alumina to aluminum sulfate in the above three experiments are compared for various temperature, $SO_2$ concentration, residence time, and particle size.

- Temperature.

As shown in FIG. 28, over the temperature range from 200 °C to 750 °C , sulfation with oxygen /ozone gave the highest absorption of $SO_2$, followed by sulfation with oxygen in the presence of UV radiation, while sulfation with oxygen only had the lowest absorption. On the other hand, sulfation with oxygen/ ozone and sulfation with oxygen in the presence of UV radiation attain maximum % absorption at about the same temperature, implying that there might be some similarity between the reaction kinetics of these two sulfation experiments.

The maximum conversion for sulfation with oxygen only is about 0.7% in 640 °C. This is in qualitative agreement with the study of Paul et al. (13). He reported that the reaction rate of $AL_2O_3$ with $SO_2$ in air was very slow-of the order of 0.04% per minute , at $SO_2$ concentration of 14 ppm and 33.1 mg of $AL_2O_3$.

-$SO_2$ Concentration

As shown in FIG. 29, $SO_2$ concentration has a more pronounced effect on sulfation with $O_2$/ $O_3$ than the others. The conversion of alumina increases with increasing

FIGURE 28. PARTICLE SIZE- CONVERSION DATA

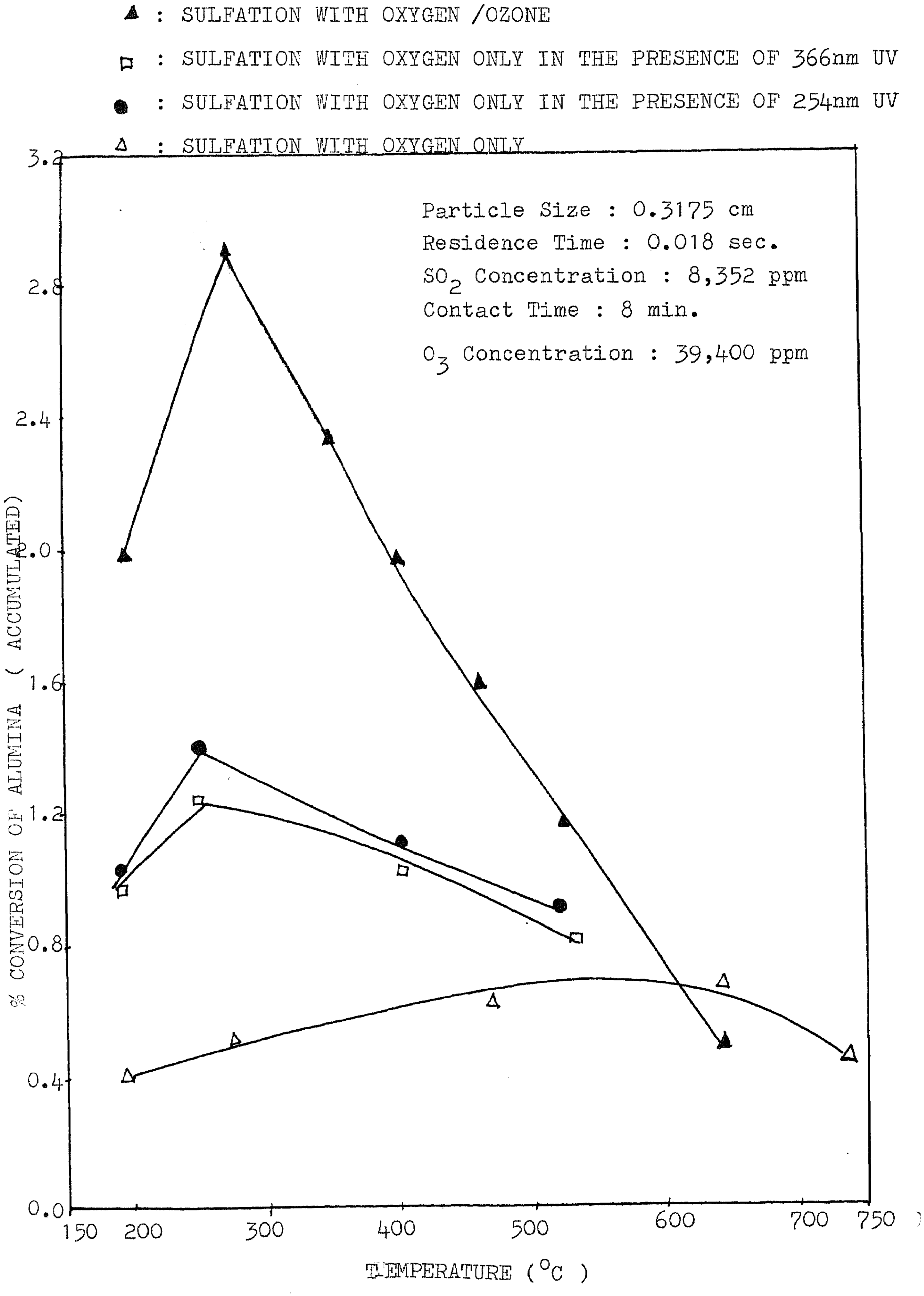


FIGURE 29. $SO_2$ CONCENTRATION- CONVERSION DATA

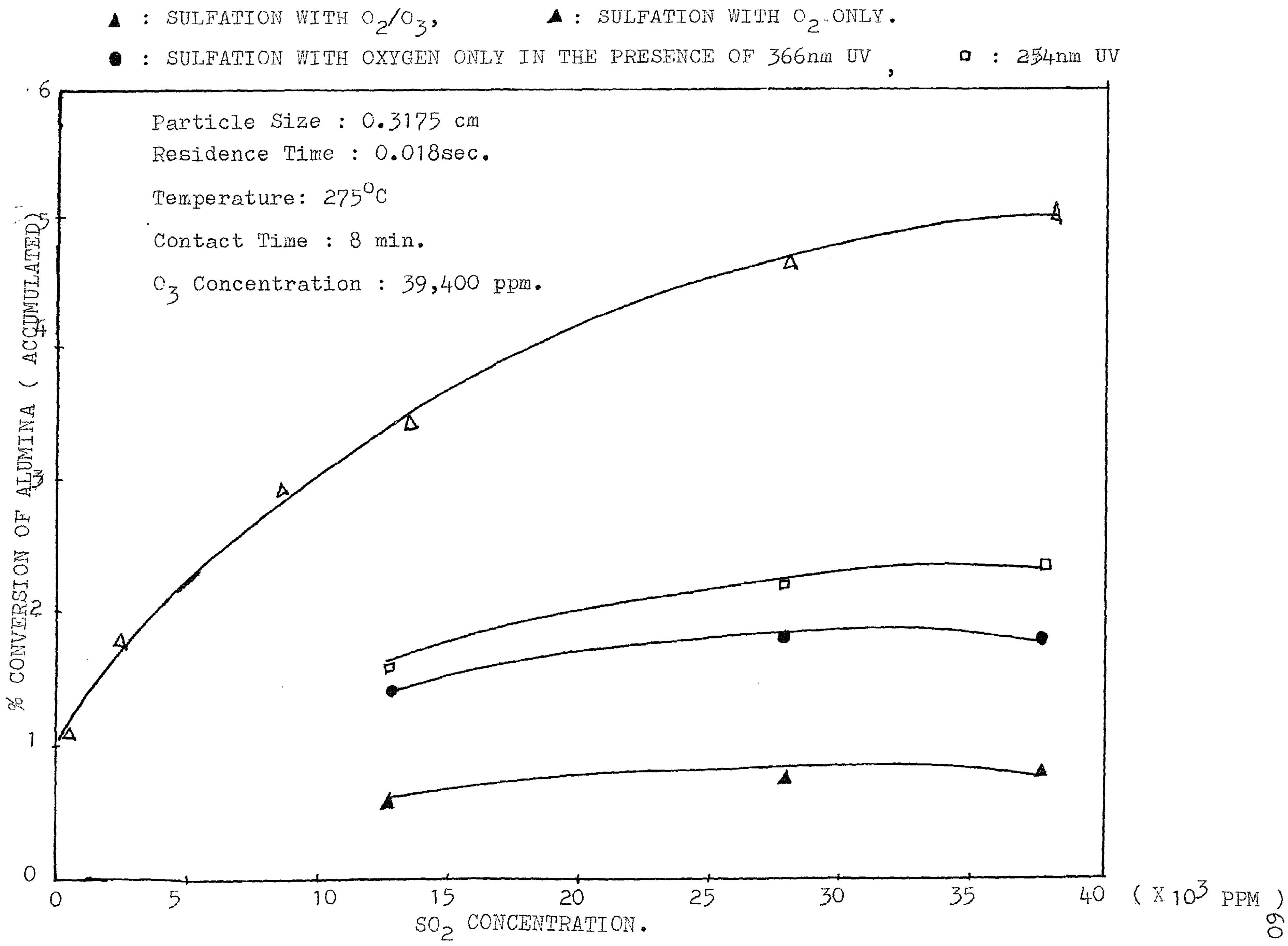


FIGURE 30. RESIDENCE TIME - CONVERSION DATA

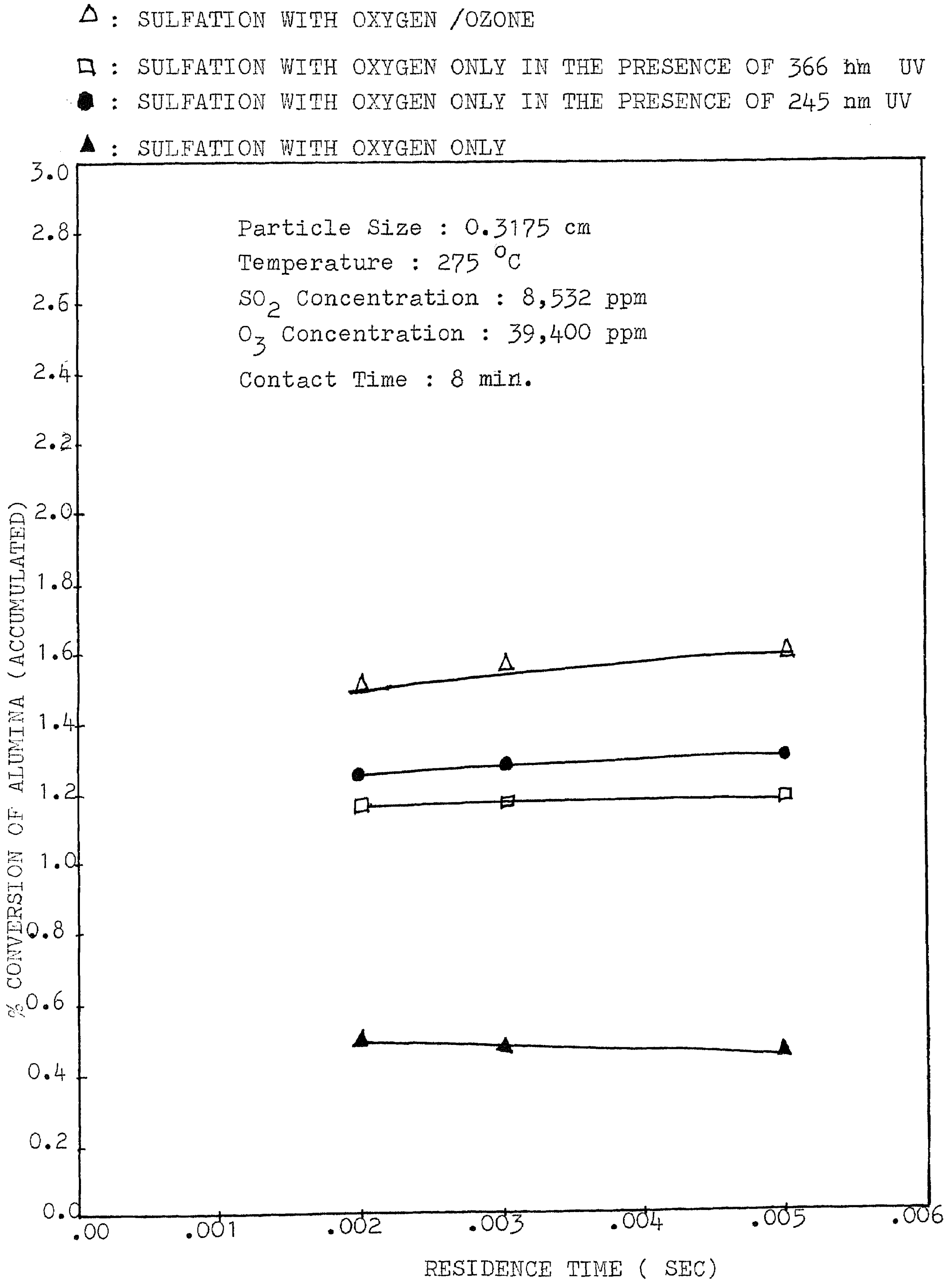
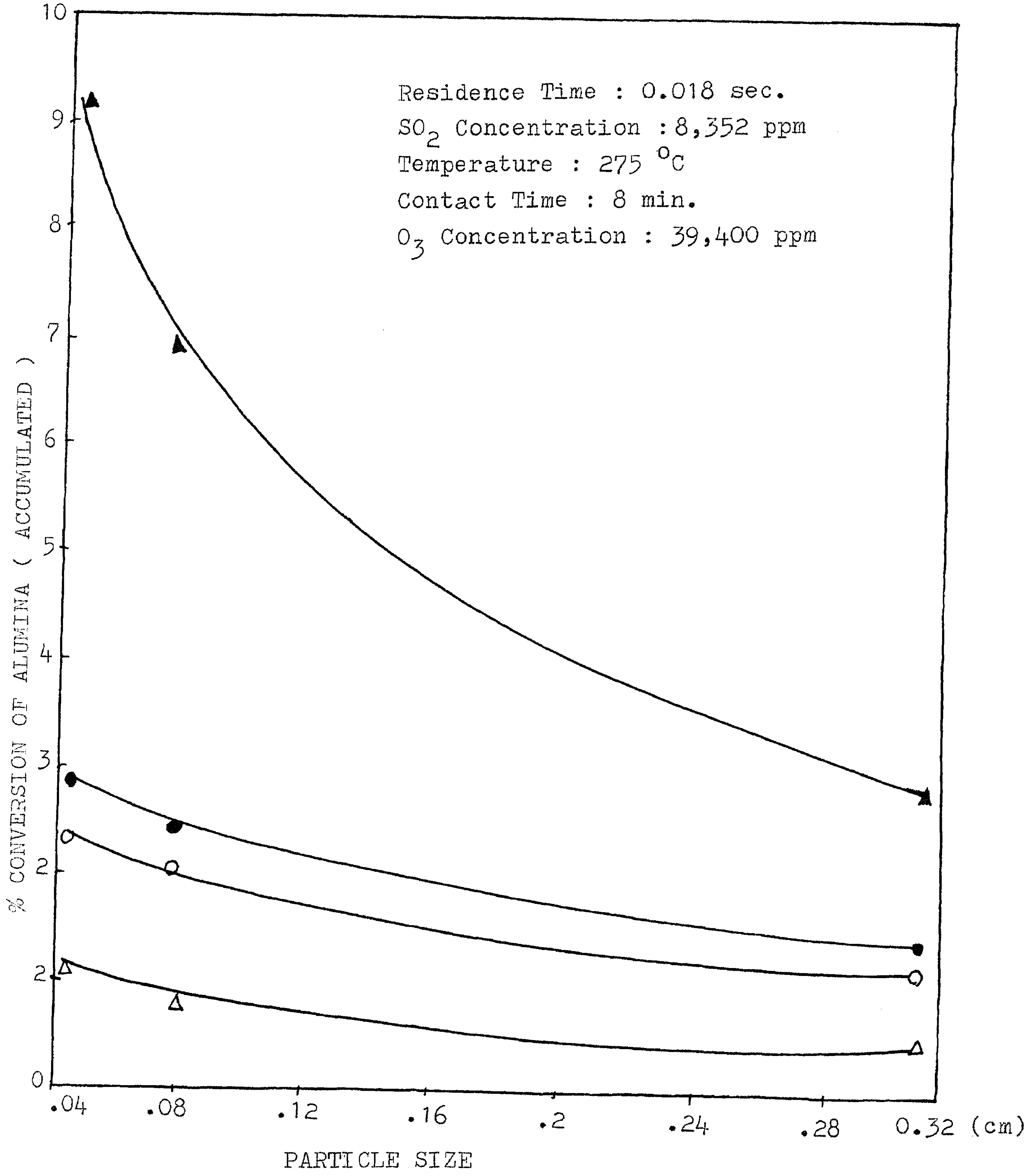


FIGURE 31. PARTICLE SIZE - CONVERSION DATA

▲ : SULFATION WITH $O_2/O_3$ , △ : SULFATION WITH $O_2$ ONLY.

○ : SULFATION WITH $O_2$ IN THE PRESENCE OF 366 nm UV RADIATION.

● : SULFATION WITH $O_2$ IN THE PRESENCE OF 254 nm UV RADIATION.



$SO_2$ concentration in all three experiments.

-Residence Time

As shown in FIG. 30, the %conversion of alumina in the reactions is almost insensitive to residence time over the range of 0.002 to 0.005 sec.. The reason for using small residence time in this study was to ensure that the measured absorption rate was not influenced by mass transfer to the surface of solid . By using small samples ( about 0.17 gram ) of 0.3175 cm spherical particles, a residence time range from 0.002 sec to 0.005 sec was obtained corresponding to a velocity from 720 cm/sec to 228 cm/sec.. In a study of the reaction of sulfur dioxide with limestone, Bougwardt (18) reported that increasing the velocity from 225 cm/sec to 2400cm/sec will increase the extent of sulfation by 5%. The negligable effect of gas velocity on %conversion implies the rate of absorption was not limited by mass transfer to solid surface.

- Particle Size

As shown in FIG. 31, particle size has a more pronounced effect on the sulfation with oxygen/ozone than on the other two sulfation experiments. Since for a given mass of alumina particles the total exterior surface increases with decreasing particle size, the increase in % absorption with small particles in all three experiments would imply that gas- solid reaction on the exterior suface seems to account considerably the absorption of $SO_2$ .

# CONCLUSION

(1) In contrast to previous studies by other investigators, highly porous aluminum oxide pellet, with effective surface area of 390 $m^2/g$, have been shown to exhibit substantial absorptive affinity for sulfur dioxide in ppm concentration level typically found in flue gas.

(2) The presence of ozone, up to about 4 % by volume, considerably promotes absorption of sulfur dioxide by alumina pellet, as compared with sulfation involving oxygen only under similar conditions.

(3) The presence of UV radiation (254 nm or 366 nm) effects some improvement of sulfur dioxide absorption using pure oxygen only. Furthermore, sulfation involving UV radiation and sulfation with oxygen/ozone exhibit some similarity in absorption charateristics, impling that they have certain features of reaction kinetics in common.

(4) Over the gas velocity range from 720 cm/sec to 228 cm/sec studied external mass transfer resistance has only negligible effect on the absorption rate.

(5) The absorption rate is very fast initially for fresh pellet and then it gradually deteriorates apparantly due to considerable pore closure by the reaction product.

# APPENDIX

## From TABLE 3 to TABLE 19

a = Weight increase (gram)

b = % conversion of $AL_2O_3$ (accumulated)

c = % absorption of $SO_2$ pergram of alumina

TABLE 3

| | | | | | | |
|---|---|---|---|---|---|---|
| RUN NUMBER | | 1 | | | 2 | |
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 39,400 | | | 39,400 | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 464 | | | 2320 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1370 | | | 0.1438 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0019 | 0.58 | 100 | 0.0023 | 0.67 | 100 |
| 2 | 0.0007 | 0.79 | 100 | 0.0014 | 1.08 | 100 |
| 3 | 0.0004 | 0.91 | 100 | 0.0010 | 1.37 | 100 |
| 4 | 0.0003 | 1.00 | 100 | 0.0007 | 1.57 | 100 |
| 5 | 0.0002 | 1.03 | 100 | 0.0004 | 1.69 | 100 |
| 6 | 0.0000 | 1.03 | ... | 0.0002 | 1.74 | 56.3 |
| 7 | 0.0000 | 1.03 | ... | 0.0001 | 1.77 | 28.2 |
| 8 | 0.0001 | 1.06 | 47.77 | 0.0000 | 1.77 | 0.00 |

# TABLE 4

| RUN NUMBER | 3 | | | 4 | | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | XXX | | | XXX | | |
| OZONE CONCENTRATION (ppm) | 39,400 | | | 39,400 | | |
| TEMPERATURE OF REACTOR ($^{o}$c) | 275 | | | 275 | | |
| PARTICLE SIZE (cm) | 0.3175 | | | 0.3175 | | |
| $SO_2$ CONCENTRATION (ppm) | 8352 | | | 13920 | | |
| RESIDENCE TIME (sec) | 0.018 | | | 0.018 | | |
| SAMPLE WEIGHT (gram) | 0.1750 | | | 0.1500 | | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0050 | 1.24 | 100 | 0.0051 | 1.44 | 100 |
| 2 | 0.0023 | 1.81 | 100 | 0.0021 | 2.03 | 93.9 |
| 3 | 0.0018 | 2.25 | 100 | 0.0018 | 2.54 | 79.6 |
| 4 | 0.0010 | 2.49 | 63.6 | 0.0012 | 2.87 | 54.1 |
| 5 | 0.0007 | 2.66 | 45.1 | 0.0009 | 3.12 | 39.8 |
| 6 | 0.0006 | 2.80 | 37.1 | 0.0006 | 3.28 | 25.4 |
| 7 | 0.0004 | 2.89 | 23.9 | 0.0004 | 3.39 | 17.5 |
| 8 | 0.0001 | 2.91 | 5.30 | 0.0001 | 3.41 | 4.45 |

TABLE 5

| RUN NUMBER | | 5 | | | 6 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 39,400 | | | 39,400 | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 27840 | | | 37120 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1378 | | | 0.1596 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0057 | 1.78 | 100 | 0.0074 | 1.96 | 100 |
| 2 | 0.0036 | 2.89 | 88.3 | 0.0045 | 3.15 | 71.05 |
| 3 | 0.0023 | 3.59 | 55.7 | 0.0026 | 3.84 | 41.20 |
| 4 | 0.0015 | 4.05 | 36.6 | 0.0018 | 4.31 | 28.06 |
| 5 | 0.0008 | 4.29 | 19.1 | 0.0014 | 4.69 | 22.09 |
| 6 | 0.0006 | 4.47 | 14.3 | 0.0009 | 4.91 | 13.73 |
| 7 | 0.0004 | 4.59 | 9.55 | 0.0006 | 5.07 | 9.55 |
| 8 | 0.0002 | 4.65 | 4.77 | 0.0003 | 5.14 | 4.17 |

## TABLE 6

| RUN NUMBER | | 7 | | | 8 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 39,400 | | | 39,400 | |
| TEMPERATURE OF REACTOR ($^{o}c$) | | 350 | | | 407 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1873 | | | 0.1537 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0039 | 0.88 | 100 | 0.0028 | 0.77 | 100 |
| 2 | 0.0026 | 1.46 | 100 | 0.0019 | 1.29 | 100 |
| 3 | 0.0016 | 1.82 | 95.5 | 0.0011 | 1.59 | 79.6 |
| 4 | 0.0010 | 2.04 | 58.3 | 0.0008 | 1.81 | 58.38 |
| 5 | 0.0006 | 2.17 | 34.5 | 0.0004 | 1.92 | 29.19 |
| 6 | 0.0003 | 2.23 | 17.78 | 0.0002 | 1.97 | 14.59 |
| 7 | 0.0001 | 2.25 | 5.83 | 0.0001 | 1.99 | 5.30 |
| 8 | 0.0000 | 2.25 | 0.00 | 0.0000 | 1.99 | 0.00 |

## TABLE 7

| RUN NUMBER | | 9 | | | 10 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 39,400 | | | 39,400 | |
| TEMPERATURE OF REACTOR (°c) | | 467 | | | 520 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1685 | | | 0.1555 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0024 | 0.60 | 100 | 0.0014 | 0.38 | 100 |
| 2 | 0.0017 | 1.02 | 100 | 0.0008 | 0.59 | 55.7 |
| 3 | 0.0011 | 1.29 | 71.6 | 0.0005 | 0.72 | 34.5 |
| 4 | 0.0007 | 1.46 | 45.11 | 0.0003 | 0.80 | 21.2 |
| 5 | 0.0004 | 1.56 | 29.19 | 0.0001 | 0.82 | 7.16 |
| 6 | 0.0002 | 1.61 | 13.26 | 0.0000 | 0.82 | 0.00 |
| 7 | 0.0000 | 1.61 | 0.00 | 0.0000 | 0.82 | 0.00 |

TABLE 8

| RUN NUMBER | | 11 | | | 12 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 39,400 | | | 39,400 | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 647 | | | 194 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1695 | | | 0.1575 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0011 | 0.27 | 71.6 | 0.0026 | 0.70 | 100 |
| 2 | 0.0006 | 0.42 | 39.8 | 0.0018 | 1.18 | 100 |
| 3 | 0.0003 | 0.49 | 18.59 | 0.0011 | 1.47 | 76.96 |
| 4 | 0.0001 | 0.515 | 6.63 | 0.0008 | 1.68 | 55.7 |
| 5 | 0.0000 | 0.515 | 0.00 | 0.0005 | 1.81 | 35.5 |
| 6 | 0.0000 | 0.515 | 0.00 | 0.0003 | 1.89 | 21.23 |
| 7 | 0.0000 | 0.515 | 0.00 | 0.0002 | 1.94 | 13.26 |
| 8 | | | | 0.0001 | 1.96 | 5.30 |

## TABLE 9

| | | | | | | |
|---|---|---|---|---|---|---|
| RUN NUMBER | | 13 | | | 14 | |
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 39,400 | | | 39,400 | |
| TEMPERATURE OF REACTOR (°c) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.0833 | | | 0.0495 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1711 | | | 0.1605 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0072 | 1.78 | 100 | 0.0094 | 2.5 | 100 |
| 2 | 0.0061 | 3.29 | 100 | 0.0075 | 4.48 | 100 |
| 3 | 0.0052 | 4.58 | 100 | 0.0060 | 6.06 | 100 |
| 4 | 0.0040 | 5.57 | 100 | 0.0047 | 7.30 | 100 |
| 5 | 0.0028 | 6.26 | 100 | 0.0035 | 8.22 | 100 |
| 6 | 0.0016 | 6.65 | 100 | 0.0022 | 8.80 | 100 |
| 7 | 0.0008 | 6.85 | 50.42 | 0.0013 | 9.14 | 90.2 |
| 8 | 0.0003 | 6.91 | 18.57 | 0.0006 | 9.29 | 39.8 |

# TABLE 10

| RUN NUMBER | | 15 | | | 16 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 32,600 | | | 26,800 | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1712 | | | 0.1787 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0046 | 1.14 | 100 | 0.0042 | 0.99 | 100 |
| 2 | 0.0021 | 1.66 | 100 | 0.0019 | 1.44 | 100 |
| 3 | 0.0017 | 2.08 | 100 | 0.0013 | 1.74 | 79.61 |
| 4 | 0.0010 | 2.32 | 63.6 | 0.0009 | 1.95 | 55.70 |
| 5 | 0.0007 | 2.49 | 45.1 | 0.0007 | 2.11 | 42.4 |
| 6 | 0.0005 | 2.61 | 32.6 | 0.0003 | 2.28 | 18.5 |
| 7 | 0.0002 | 2.66 | 13.0 | 0.0001 | 2.33 | 5.30 |
| 8 | 0.0001 | 2.68 | 5.36 | 0.0000 | 2.33 | 0.00 |

## TABLE 11

| RUN NUMBER | | 17 | | | 18 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 10,296 | | | 12,000 | |
| TEMPERATURE OF REACTOR (°c) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.005 | |
| SAMPLE WEIGHT (gram) | | 0.1915 | | | 0.1902 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0039 | 0.86 | 100 | 0.0037 | 0.82 | 100 |
| 2 | 0.0018 | 1.25 | 100 | 0.0015 | 1.15 | 87.5 |
| 3 | 0.0011 | 1.49 | 63.6 | 0.0011 | 1.39 | 63.69 |
| 4 | 0.0009 | 1.68 | 50.4 | 0.0008 | 1.56 | 45.11 |
| 5 | 0.0006 | 1.81 | 35.2 | 0.0004 | 1.65 | 23.61 |
| 6 | 0.0003 | 1.88 | 17.51 | 0.0002 | 1.69 | 11.67 |
| 7 | 0.0000 | 1.88 | 0.000 | 0.0001 | 1.71 | 5.83 |
| 8 | | | | 0.0000 | 1.71 | 0.00 |

TABLE 12

| RUN NUMBER | | 19 | | | 20 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | 12,000 | | | 12,00 | |
| TEMPERATURE OF REACTOR ($^{o}c$) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.003 | | | 0.002 | |
| SAMPLE WEIGHT (gram) | | 0.1931 | | | 0.1605 | |
| TIME (min) | a | b | c | a | b | c |
| 1 | 0.0029 | 0.63 | 100 | 0.0026 | 0.68 | 100 |
| 2 | 0.0019 | 1.04 | 100 | 0.0014 | 1.05 | 98.1 |
| 3 | 0.0012 | 1.30 | 69.0 | 0.0009 | 1.28 | 61.0 |
| 4 | 0.0007 | 1.45 | 39.8 | 0.0005 | 1.41 | 34.5 |
| 5 | 0.0004 | 1.53 | 21.2 | 0.0004 | 1.51 | 26.53 |
| 6 | 0.0002 | 1.57 | 10.6 | 0.0002 | 1.56 | 13.26 |
| 7 | 0.0001 | 1.59 | 5.3 | 0.0000 | 1.56 | 0.00 |
| 8 | 0.0000 | 1.59 | 0.00 | | | |

TABLE 13

| | | | | | | |
|---|---|---|---|---|---|---|
| RUN NUMBER | | 21 | | | 22 | |
| UV LIGHT WAVE LENGTH (nm) | | 254 | | | 254 | |
| OZONE CONCENTRATION (ppm) | | XXX | | | XXX | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 275 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.1692 | | | 0.1880 | |
| TIME (min) | a | b | c | a | b | c |
| 0.5 | 0.0026 | 0.65 | 100 | 0.0020 | 0.45 | 100 |
| 1 | 0.0013 | 0.97 | 100 | 0.0012 | 0.72 | 100 |
| 2 | 0.0009 | 1.19 | 58.3 | 0.0008 | 0.90 | 47.77 |
| 3 | 0.0006 | 1.34 | 39.8 | 0.0004 | 0.99 | 23.88 |
| 4 | 0.0002 | 1.39 | 13.2 | 0.0001 | 1.01 | 5.30 |
| 6 | 0.0000 | 1.39 | 0.00 | 0.0000 | 1.01 | 0.00 |

# TABLE 14

| RUN NUMBER | 23 | | | 24 | | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | 254 | | | 254 | | |
| OZONE CONCENTRATION (ppm) | XXX | | | XXX | | |
| TEMPERATURE OF REACTOR ($^{o}$c) | 520 | | | 194 | | |
| PARTICLE SIZE (cm) | 0.3175 | | | 0.3175 | | |
| $SO_2$ CONCENTRATION (ppm) | 8352 | | | 8352 | | |
| RESIDENCE TIME (sec) | 0.018 | | | 0.018 | | |
| SAMPLE WEIGHT (gram) | 0.1613 | | | 0.1580 | | |
| TIME (min) | a | b | c | a | b | c |
| 0.5 | 0.0016 | 0.42 | 100 | 0.0018 | 0.48 | 100 |
| 1 | 0.0010 | 0.68 | 100 | 0.0011 | 0.77 | 100 |
| 2 | 0.0006 | 0.83 | 39.8 | 0.0007 | 0.95 | 47.77 |
| 3 | 0.0003 | 0.90 | 18.5 | 0.0003 | 1.03 | 21.22 |
| 4 | 0.0000 | 0.90 | 0.00 | 0.0001 | 1.05 | 5.3 |
| 6 | | | | 0.0000 | 1.05 | 0.00 |

## TABLE 15

| | | | | | | |
|---|---|---|---|---|---|---|
| RUN NUMBER | | 25 | | | 26 | |
| UV LIGHT WAVE LENGTH (nm) | | 366 | | | 366 | |
| OZONE CONCENTRATION (ppm) | | XXX | | | XXX | |
| TEMPERATURE OF PEACTOR (°c) | | 275 | | | 407 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.2010 | | | 0.1900 | |
| TIME (min) | a | b | c | a | b | c |
| 0.5 | 0.0026 | 0.54 | 100 | 0.0022 | 0.49 | 100 |
| 1 | 0.0014 | 0.83 | 100 | 0.0013 | 0.78 | 100 |
| 2 | 0.0010 | 1.04 | 55.73 | 0.0009 | 0.98 | 53.0 |
| 3 | 0.0007 | 1.18 | 37.15 | 0.0004 | 1.07 | 23.8 |
| 4 | 0.0003 | 1.24 | 15.92 | 0.0002 | 1.11 | 10.6 |
| 6 | 0.0001 | 1.26 | 5.30 | 0.0000 | 1.11 | 0.00 |
| 8 | 0.0000 | 1.26 | 0.00 | | | |

# TABLE 16

| RUN NUMBER | | 27 | | | 28 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | 366 | | | 366 | |
| OZONE CONCENTRATION (ppm) | | XXX | | | XXX | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 520 | | | 194 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.2019 | | | 0.1980 | |
| TIME (min) | a | b | c | a | b | c |
| 0.5 | 0.0018 | 0.37 | 100 | 0.0021 | 0.45 | 100 |
| 1 | 0.0011 | 0.60 | 100 | 0.0013 | 0.72 | 100 |
| 2 | 0.0007 | 0.74 | 37.15 | 0.0008 | 0.89 | 45.11 |
| 3 | 0.0003 | 0.80 | 15.9 | 0.0004 | 0.97 | 21.23 |
| 4 | 0.0001 | 0.82 | 5.30 | 0.0001 | 0.99 | 5.30 |
| 6 | 0.0000 | 0.82 | 0.00 | 0.0000 | 0.99 | 5.30 |

## TABLE 17

| RUN NUMBER | | 29 | | | 30 | |
|---|---|---|---|---|---|---|
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | XXX | | | XXX | |
| TEMPERATURE OF REACTOR ($^{o}$c) | | 194 | | | 275 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.2055 | | | 0.1904 | |
| TIME (min) | a | b | c | a | b | c |
| 0.5 | 0.0011 | 0.22 | 100 | 0.0011 | 0.24 | 100 |
| 1 | 0.0006 | 0.34 | 63.69 | 0.0006 | 0.37 | 69.0 |
| 2 | 0.0003 | 0.40 | 15.92 | 0.0004 | 0.45 | 21.23 |
| 3 | 0.0001 | 0.42 | 5.30 | 0.0002 | 0.49 | 10.6 |
| 4 | 0.0000 | 0.42 | 0.00 | 0.0001 | 0.51 | 5.30 |
| 6 | | | | 0.0000 | 0.51 | 0.00 |

## TABLE 18

| | | | | | | |
|---|---|---|---|---|---|---|
| RUN NUMBER | | 31 | | | 32 | |
| UV LIGHT WAVE LENGTH (nm) | | XXX | | | XXX | |
| OZONE CONCENTRATION (ppm) | | XXX | | | XXX | |
| TEMPERATURE OF REACTOR ($^o$c) | | 468 | | | 640 | |
| PARTICLE SIZE (cm) | | 0.3175 | | | 0.3175 | |
| $SO_2$ CONCENTRATION (ppm) | | 8352 | | | 8352 | |
| RESIDENCE TIME (sec) | | 0.018 | | | 0.018 | |
| SAMPLE WEIGHT (gram) | | 0.2025 | | | 0.1945 | |
| TIME (min) | a | b | c | a | b | c |
| 0.5 | 0.0012 | 0.25 | 100 | 0.0015 | 0.32 | 100 |
| 1 | 0.0007 | 0.40 | 79.6 | 0.0008 | 0.49 | 90.2 |
| 2 | 0.0004 | 0.48 | 21.3 | 0.0005 | 0.59 | 26.5 |
| 3 | 0.0003 | 0.54 | 15.9 | 0.0004 | 0.67 | 21.2 |
| 4 | 0.0002 | 0.58 | 10.6 | 0.0002 | 0.71 | 10.6 |
| 6 | 0.0000 | 0.58 | 0.00 | 0.0000 | 0.71 | 0.00 |

TABLE 19

| | |
|---|---|
| RUN NUMBER | 33 |
| UV LIGHT WAVE LENGTH (nm) | XXX |
| OZONE CONCENTRATION (ppm) | XXX |
| TEMPERATURE OF REACTOR ($^{o}$c) | 730 |
| PARTICLE SIZE (cm) | 0.3175 |
| $SO_2$ CONCENTRATION (ppm) | 8352 |
| RESIDENCE TIME (sec) | 0.018 |
| SAMPLE WEIGHT (gram) | 0.1823 |

| TIME (min) | a | b | c |
|---|---|---|---|
| 0.5 | 0.0009 | 0.20 | 100 |
| 1 | 0.0005 | 0.32 | 63.6 |
| 2 | 0.0004 | 0.41 | 23.8 |
| 3 | 0.0002 | 0.45 | 11.9 |
| 4 | 0.0001 | 0.47 | 5.30 |
| 6 | 0.0000 | 0.47 | 0.00 |

# REFERENCES

( 1) Felder, R. M. and Rosseau, R. W., " Elementary Principles of Chemical Process ", John Wily and sons. N. Y. 1978

( 2) Stewart, R. D., " The Application of Dry Solid Metal Oxide Sorbents to Utility Boiler $SO_2$ Removal Process with Sulfur Recovery", N. J. I. T. 1978

( 3) McCarthy, J. E. " Choosing a Flue- Gas Desulfurization System ', Chem. Eng., March, p.79

( 4) Murthy, K. S. , Rosenberg, H. S., Engdahl, R. B., " Status and Problems of Regenerable Flue gas Desulfurization Processes ", Journal of Air Pollution Control Association, vol. 26, no. 9 (1976)

( 5) Lowell, P. S., Davis, D. L., ' Application of Metal Oxides to the Development of New Processes for Removing $SO_2$ from Flue Gases", Tracer Inc., Final Report-NAPCA Contract-p-1-66-68-68, July, 1969

( 6) McCrea, D. H., Forney, A. J., Myers, J. G., " Recov-ery of Flue Gases Using a Copper Oxide Adsorbent, JAPCA vol. 20, no. 12, Sept. 1970

( 7) Zanders, D., Opferkuch, R.,-Monsanto, " Applicability of Commercially Available Catalysts for Removing $SO_2$ from Flue Gases", JAPCA, vol.24, no. 3 March 1974

( 8) Toscano, J. " $SO_3$ Adsorption Experiments", N. J. I. T. , Project Data Sheets, 1974.

( 9) Nejat Yildirim, " The Removal of $SO_2$ From Stack Gases using Aluminum Oxide in a Dry Process", N. J. I T. 1980.

(10) Ramachandran, P. A., Smith, J. M., " A Single Pore Model for Gas-Solid Noncatalytic Reactions ", AICHE Journal,23, no3,May 1977.

(11)G Noickless, " inorganic Sulfur Chemistry ", p 375.

(12) Cullis C. F. , Henson, R. M. , Trimm, D. L., Proc. Roy Soc. 295, 72-83 1966

(13) Paul Urone, Helmut Lutsep, Clandia M. Noyes, and jon F. Parcher, " Static Studies of Sulfur Dioxide Reactions in Air", Environmemtal Science and Technology vol.2, no8, August 1968.

(14) S. M. Slatter and Mark s. Rizzon, " Futher Studies on Ozone Oxidation of $SO_2$ in an Idealized Flue Gas", AICHE Syposium Series, 1979

(15) Welsbach Basic Manual, Welsbach Ozone Systems Corporation.

(16) Slatter, S. M. and A. A. Balaco, " Ozone Oxidation of Sulfur Dioxide at Elevated Temperatures " AICHE Syposium Series, 1979

(17) Philip S. Lowell, Klaus Schwitzgebel, Terry B. Parsons, Karl J. Sladek, " Selection of Metal Oxides for Removing $SO_2$ From Flue Gas ", Ind. Eng. Chem. Process Des. Develop., vol 10, no 3, 1971

(18) R. H. Borgwardt, " Kinetics of the Reaction of $SO_2$ with Calined Linestone ", Environmental Science & Technology, vol. 4, no.1, January, 1970